SUPPLEMENTARY MATERIAL

Isolation and structural elucidation of new amphidinol analogues from *Amphidinium carterae* cultivated in a pilot scale photobioreactor

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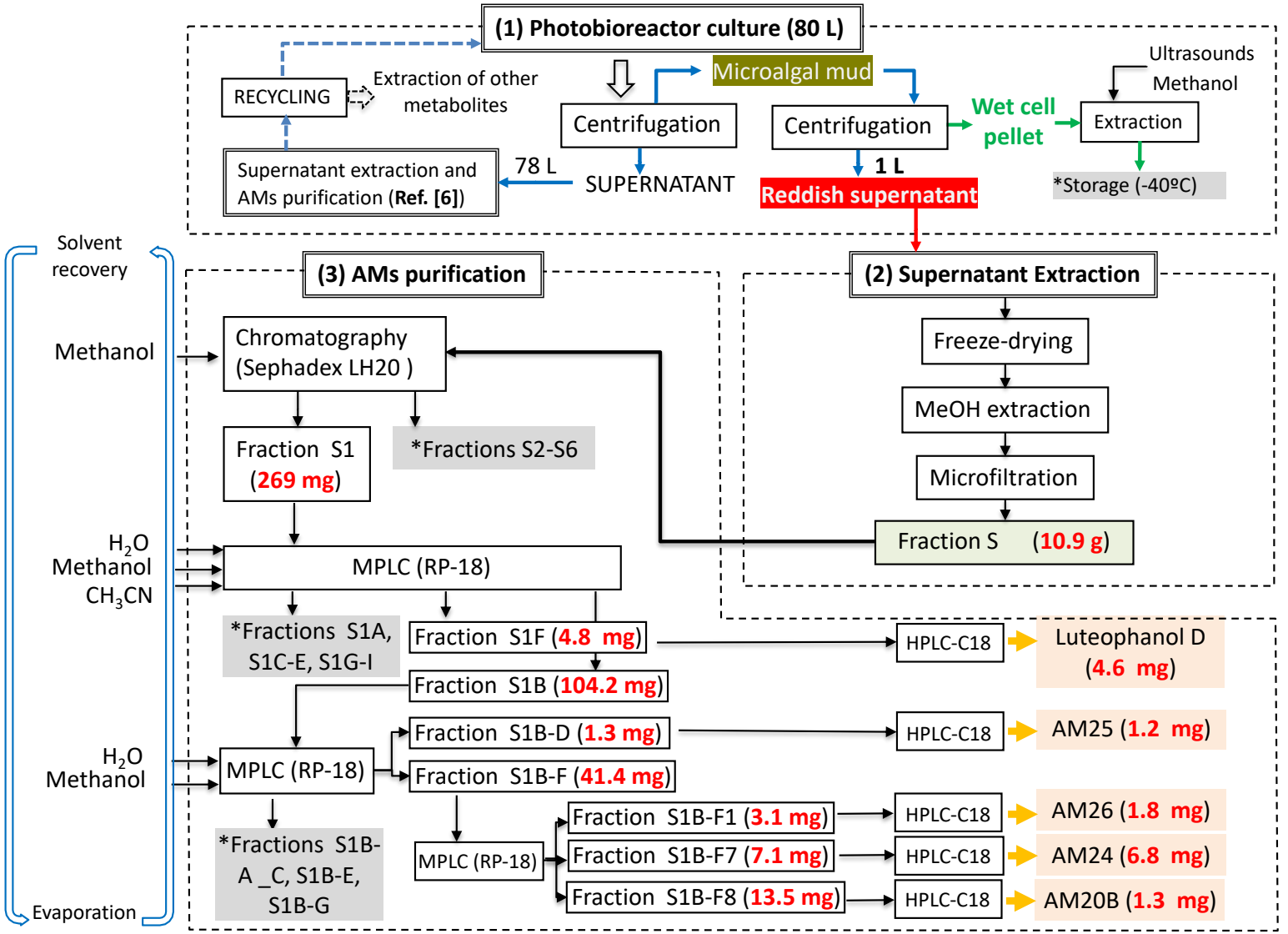
Scheme S1. Production of new amphidinol analogues by the marine microalga *Amphidinium carterae* grown in a pilot-scale LED-illuminated photobioreactor.



Scheme S2. Isolation procedure for new amphidinol analogues.

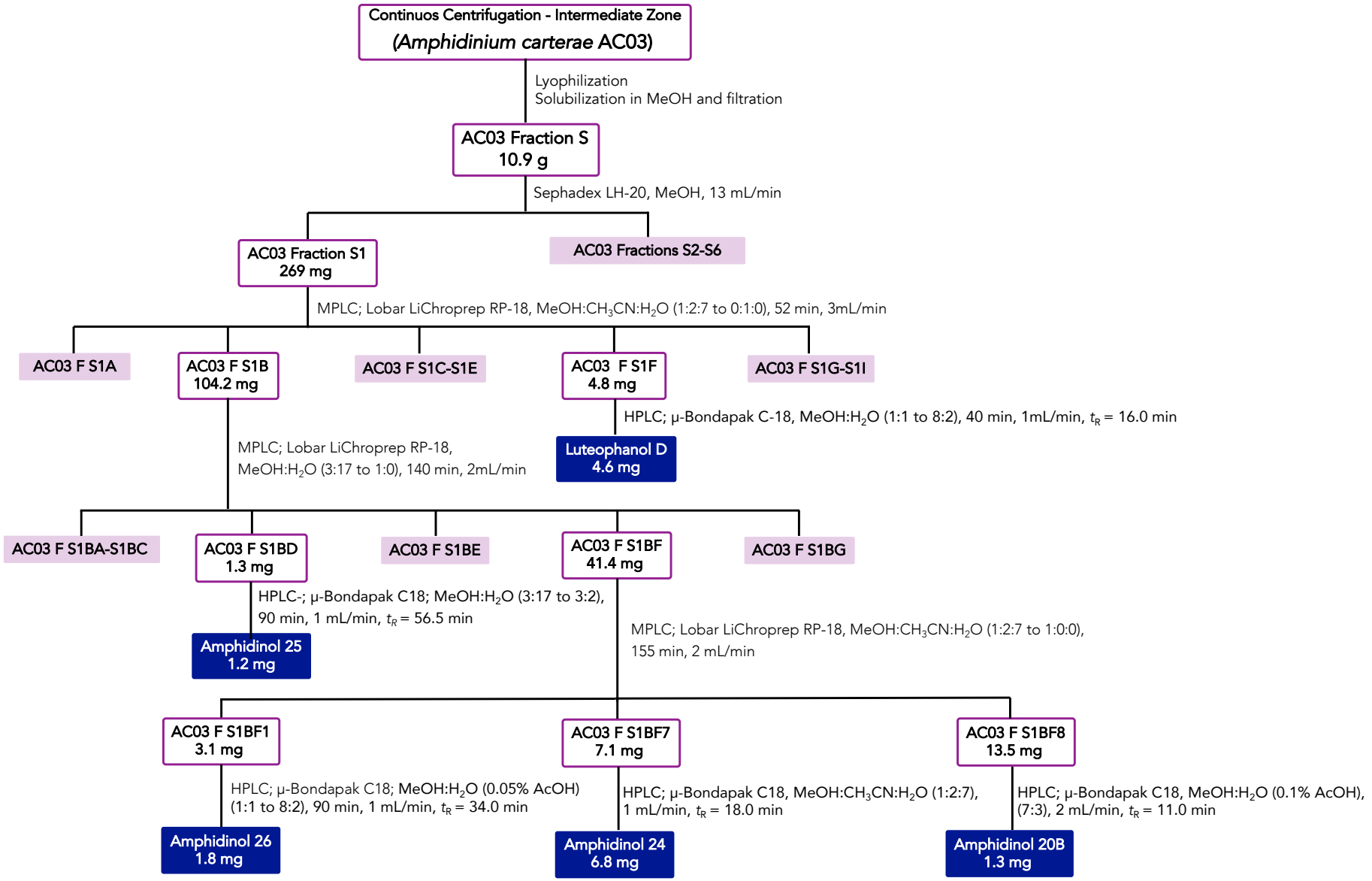


Table S1. ^{1}H and ^{13}C-NMR data (600 MHz, CD_3OD) for amphidinols 24, 25 and 27.

#	Amphidinol 24		Amphidinol 25		Amphidinol 27	
	δC, type	δH	δC, type	δH	δC, type	δH
1	67.0, CH_2	3.43; 3.48	67.1, CH_2	3.43; 3.47	67.1, CH_2	3.43; 3.48
2	73.0, CH	3.58	73.1, CH	3.59	73.1, CH	3.59
3	34.2, CH_2	1.38; 1.54	34.3, CH_2	1.37; 1.54	34.3, CH_2	1.38; 1.54
4	22.6, CH_2	1.38; 1.62	22.6, CH_2	1.38; 1.61	22.6, CH_2	1.38; 1.61
5	38.2, CH_2	1.40; 1.50	38.2, CH_2	1.40; 1.50	38.1, CH_2	1.40; 1.50
6	72.0, CH	3.54	72.1, CH	3.54	72.0, CH	3.56
7	38.2, CH_2	1.40; 1.50	38.2, CH_2	1.40; 1.50	38.1, CH_2	1.40; 1.50
8	22.6, CH_2	1.38; 1.62	22.6, CH_2	1.38; 1.61	22.6, CH_2	1.38; 1.62
9	37.6, CH_2	1.40; 1.52	37.6, CH_2	1.39; 1.52	37.7, CH_2	1.40; 1.52
10	71.9, CH	3.58	72.2, CH	3.58	72.4, CH	3.59
11	41.2, CH_2	2.20 (2H)	41.4, CH_2	2.20 (2H)	41.2, CH_2	2.19 (2H)
12	128.6, CH	5.69	128.6, CH	5.68	128.5, CH	5.70
13	136.0, CH	5.53	135.9, CH	5.53	135.9, CH	5.55
14	73.2, CH	4.05	73.3, CH	4.05	73.2, CH	4.05
15	41.7, CH_2	2.25 (2H)	41.8, CH_2	2.24 (2H)	41.7, CH_2	2.24 (2H)
16	129.7, CH	5.54	129.6, CH	5.53	129.6, CH	5.55
17	137.3, CH	5.60	130.1, CH	5.60	130.1, CH	5.60
18	37.7, CH_2	2.08; 2.48	37.7, CH_2	2.08; 2.48	37.7, CH_2	2.08; 2.48
19	72.2, CH	3.52	72.2, CH	3.52	72.1, CH	3.52
20	78.9, CH	3.52	78.7, CH	3.52	78.7, CH	3.52
21	35.0, CH	2.30	35.0, CH	2.30	34.9, CH	2.30
22	79.9, CH	3.53	79.6, CH	3.53	79.7, CH	3.53
23	71.7, CH	3.71	71.2, CH	3.71	71.7, CH	3.72
24	40.7, CH_2	1.54; 1.91	40.9, CH_2	1.53; 1.91	40.8, CH_2	1.54; 1.90
25	71.1, CH	3.86	71.1, CH	3.86	70.1, CH	3.87
26	36.2, CH_2	1.59; 1.68	37.4, CH_2	1.59; 1.68	36.2, CH_2	1.59; 1.68
27	36.8, CH_2	2.12; 2.21	36.5, CH_2	2.12; 2.21	36.4, CH_2	1.54; 1.90
28	139.0, C		139.0, C		139.1, C	
29	125.9, CH	5.48	125.9, CH	5.48	125.8, CH	5.48
30	67.6, CH	4.55	67.6, CH	4.55	67.6, CH	4.56
31	72.0, CH	3.69	72.0, CH	3.69	72.0, CH	3.68
32	78.8, CH	3.96	78.9, CH	3.97	78.8, CH	3.96
33	67.1, CH	3.97	68.4, CH	4.04	68.4, CH	4.05
34	68.4, CH	4.04	68.4, CH	3.97	67.1, CH	3.98
35	30.0, CH_2	1.79 (2H)	30.1, CH_2	1.79 (2H)	30.1, CH_2	1.79 (2H)
36	75.3, CH	3.49	75.3, CH	3.49	75.3, CH	3.49
37	74.2, CH	3.60	74.1, CH	3.60	74.1, CH	3.61
38	32.1, CH_2	1.57; 1.97	32.3 CH_2	1.57; 1.97	32.2 CH_2	1.56; 1.97
39	27.8, CH_2	2.10; 2.42	27.9, CH_2	2.10; 2.42	28.0, CH_2	2.10; 2.41
40	151.4, C		151.1, C		151.2, C	
41	76.3, CH	4.18	76.2, CH	4.18	76.1, CH	4.19
42	74.1, CH	3.35	75.0, CH	3.34	75.0, CH	3.35
43	70.0, CH	4.05	70.1, CH	4.04	70.2, CH	4.04
44	31.1 CH_2	1.56; 2.09	31.3, CH_2	1.56; 2.09	31.2, CH_2	1.56; 2.09
45	66.8, CH	4.05	67.1, CH	4.05	67.2, CH	4.05
46	68.4, CH	4.05	68.4, CH	4.04	68.4, CH	4.05
47	80.2, CH	3.74	80.3, CH	3.75	80.1, CH	3.75
48	71.6, CH	3.97	71.7, CH	3.96	71.6, CH	3.97
49	73.8, CH	4.37	73.9, CH	4.36	73.7, CH	4.37
50	128.6, CH	5.64	128.6, CH	5.63	128.5, CH	5.66
51	134.9, CH	5.80	135.0, CH	5.80	134.7, CH	5.83
52	29.3, CH_2	2.16 (2H)	29.4, CH_2	2.15 (2H)	29.4, CH_2	2.18 (2H)
53	37.6, CH_2	1.60; 1.64	37.6, CH_2	1.62 (2H)	38.8, CH	2.16 (2H)
54	72.2, CH	4.12	72.4, CH	4.11	182.8, C	
55	137.0, CH	5.69	133.8, CH	5.67	6.7, CH_3	0.97
56	130.7, CH	6.23	130.7, CH	6.23	17.1, CH_3	1.75
57	130.7, CH	6.23	130.7, CH	6.23	112.6, CH_2	4.99;
58	137.0, CH	5.69	133.8, CH	5.67		5.09
59	72.8, CH	4.10	72.4, CH	4.11		
60	34.2, CH_2	1.59; 1.71	33.7, CH_2	1.71; 1.73		
61	34.2, CH_2	1.38; 1.54	34.2, CH_2	1.71; 1.87		
62	73.0, CH	3.58	77.3, CH	4.50		
63	67.8, CH_2	3.43; 3.48	69.1, CH_2	4.10; 4.26		
64	6.6, CH_3	0.98	6.7, CH_3	0.98		
65	17.1, CH_3	1.75	17.1, CH_3	1.75		
66	112.8, CH_2	4.99; 5.08	112.7, CH_2	4.99; 5.08		

Figure S1. ^{1}H NMR spectrum (600 MHz, CD_3OD) for amphidinol 24.

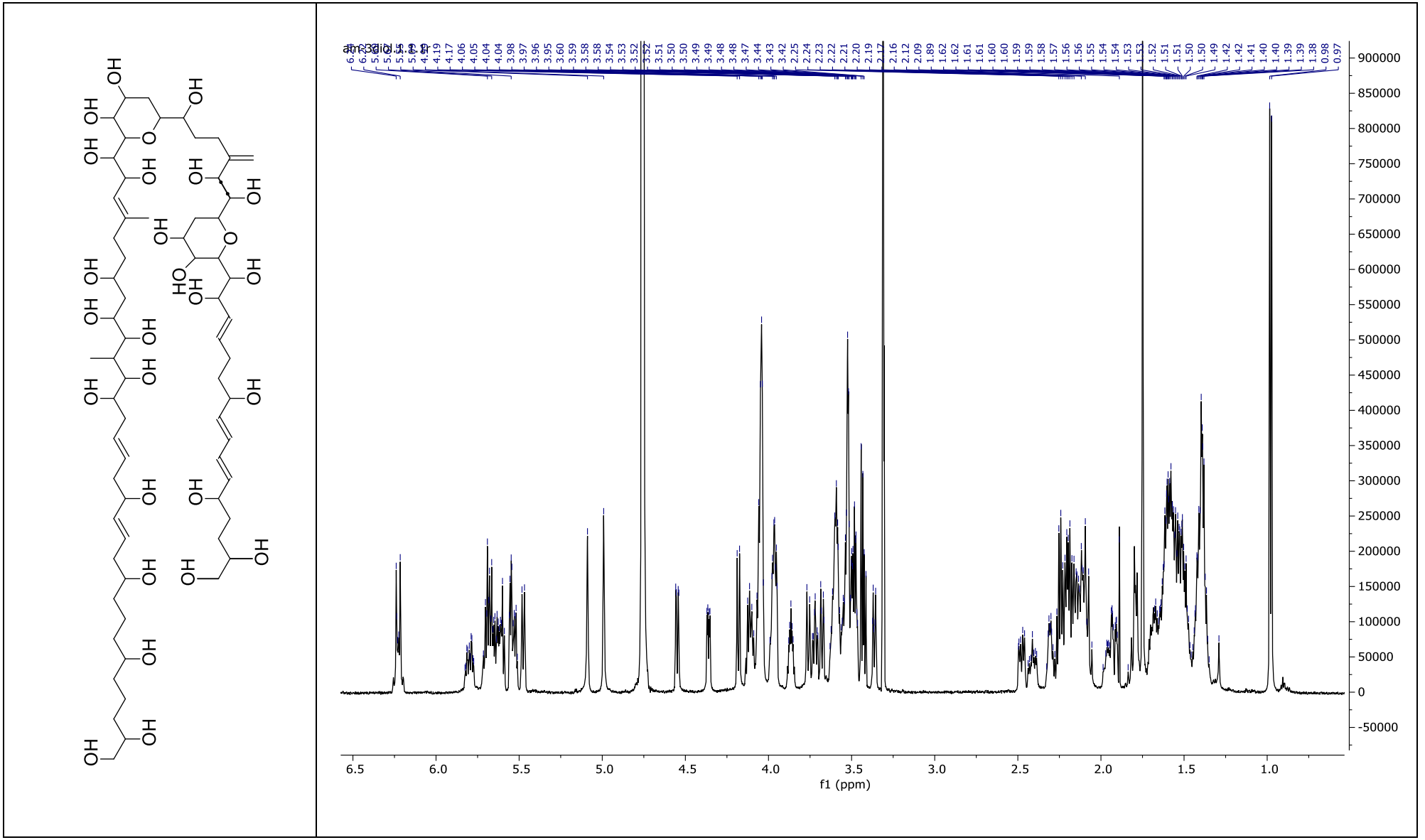


Figure S2. COSY spectrum (600 MHz, CD_3OD) for amphidinol 24.

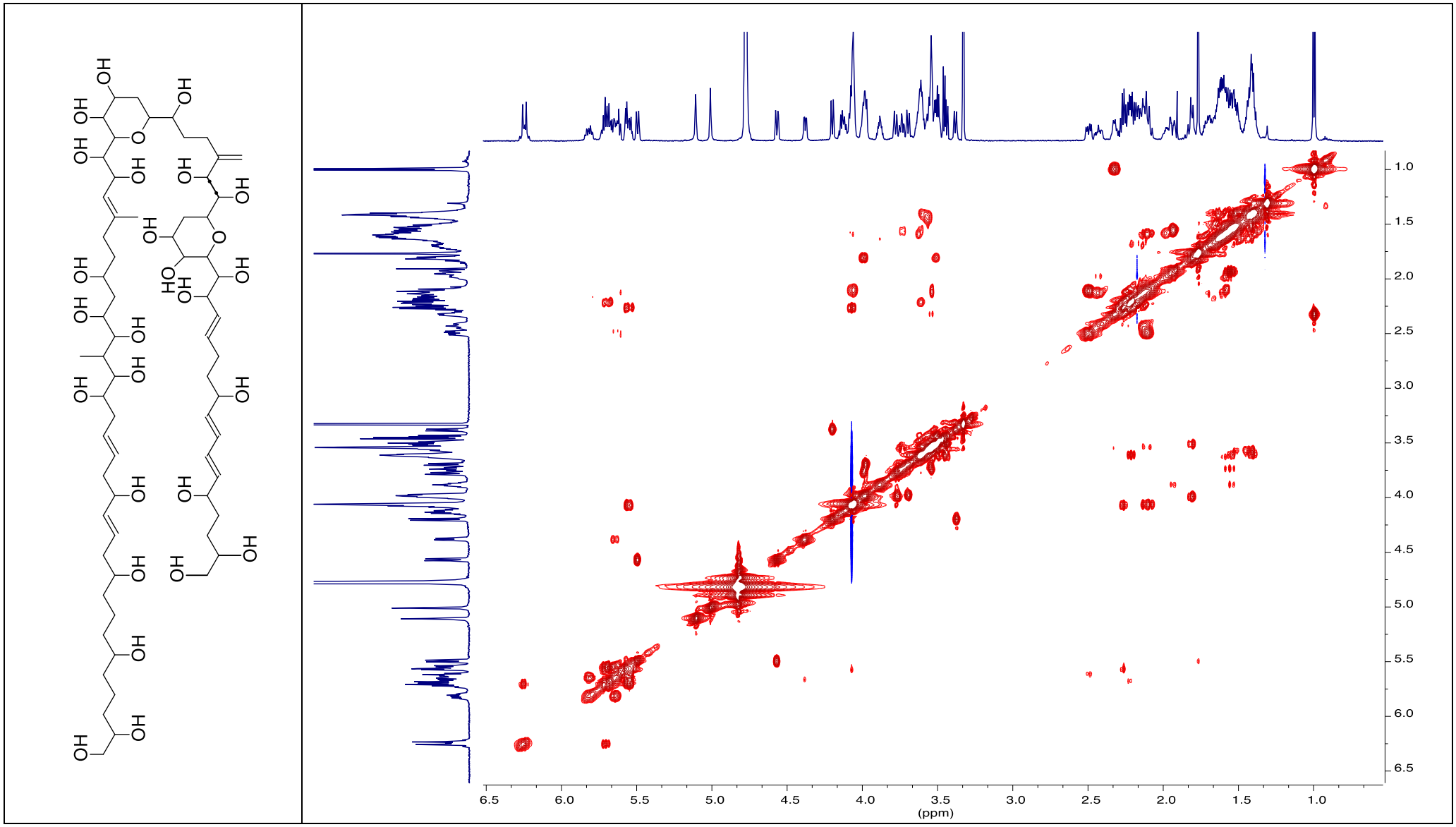


Figure S3. $HSQC_{ed}$ spectrum (600 MHz, CD_3OD) for amphidinol 24.

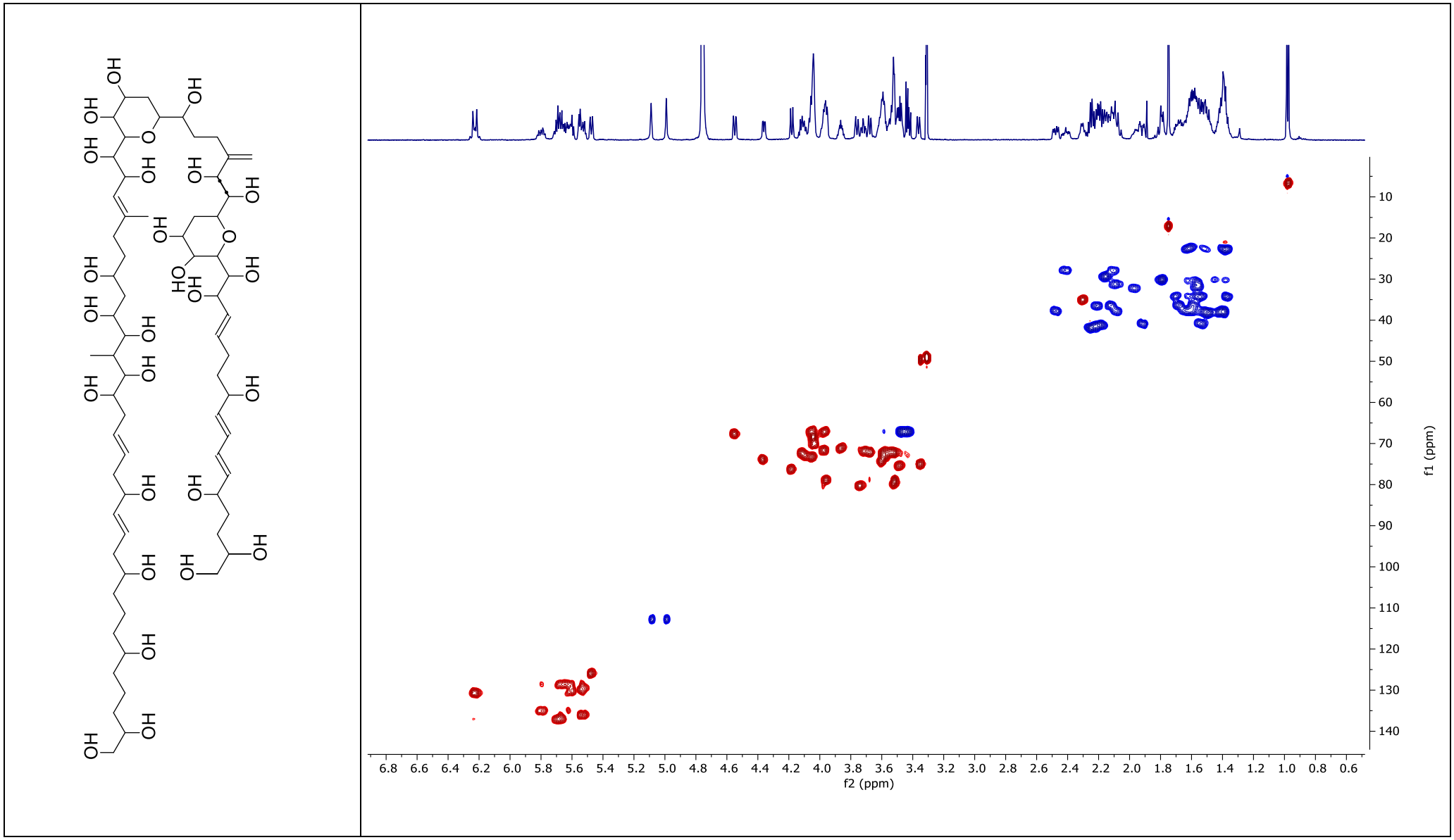


Figure S4. HSQC-TOCSY spectrum (600 MHz, CD_3OD) for amphidinol 24.

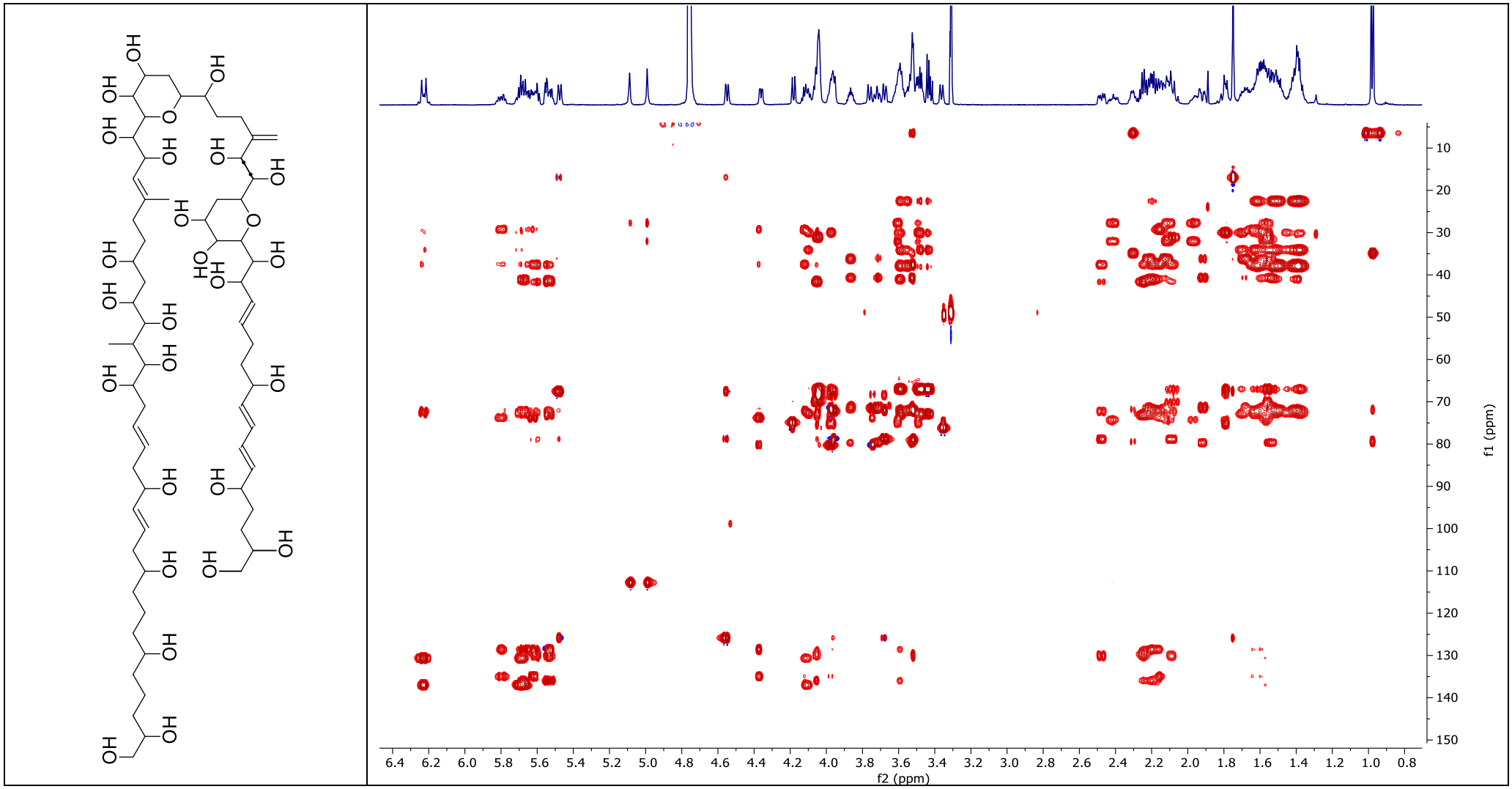


Figure S5. HMBC spectrum (600 MHz, CD_3OD) for amphidinol 24.

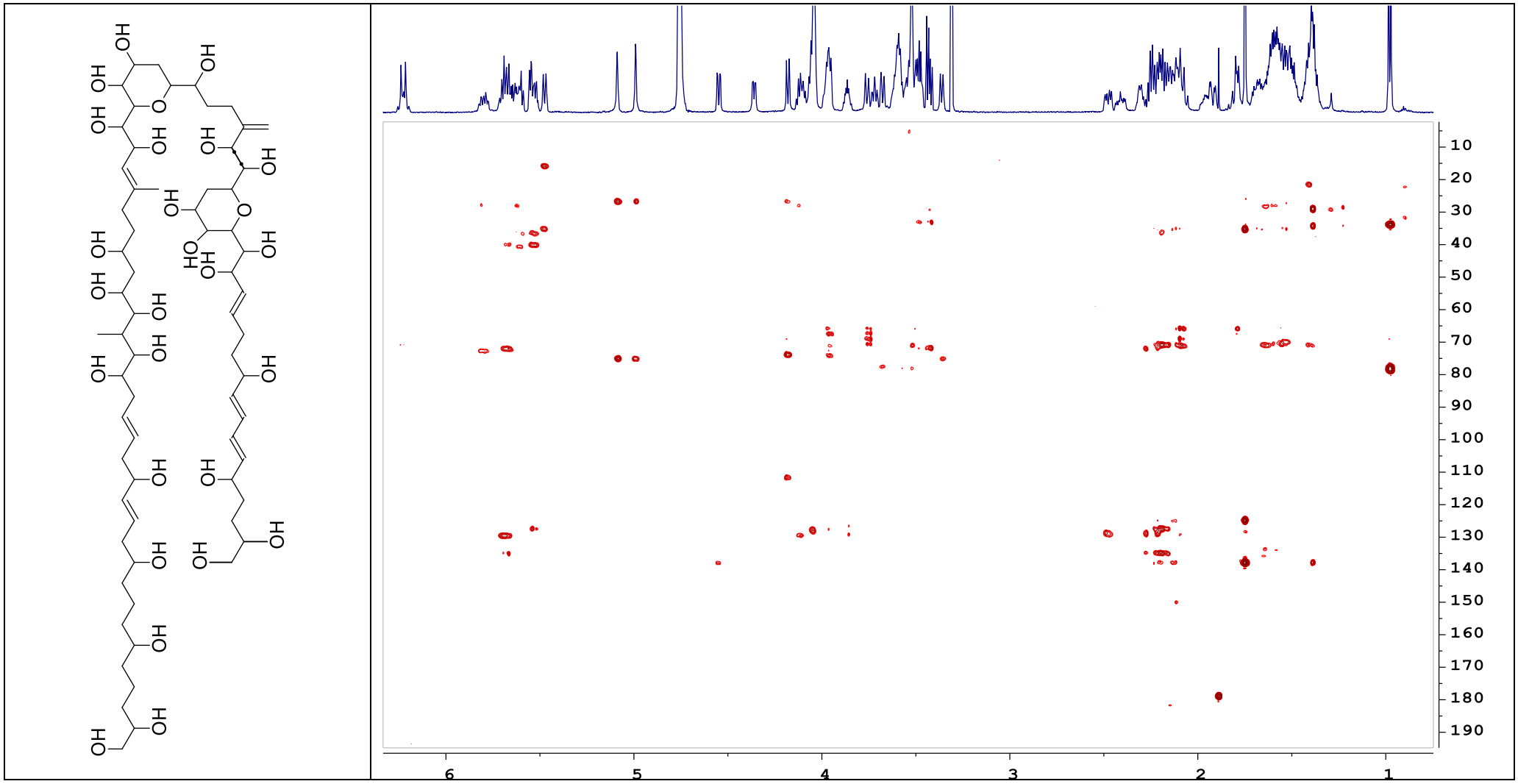


Figure S6. H2BC spectrum(600 MHz, CD_3OD) for amphidinol 24.

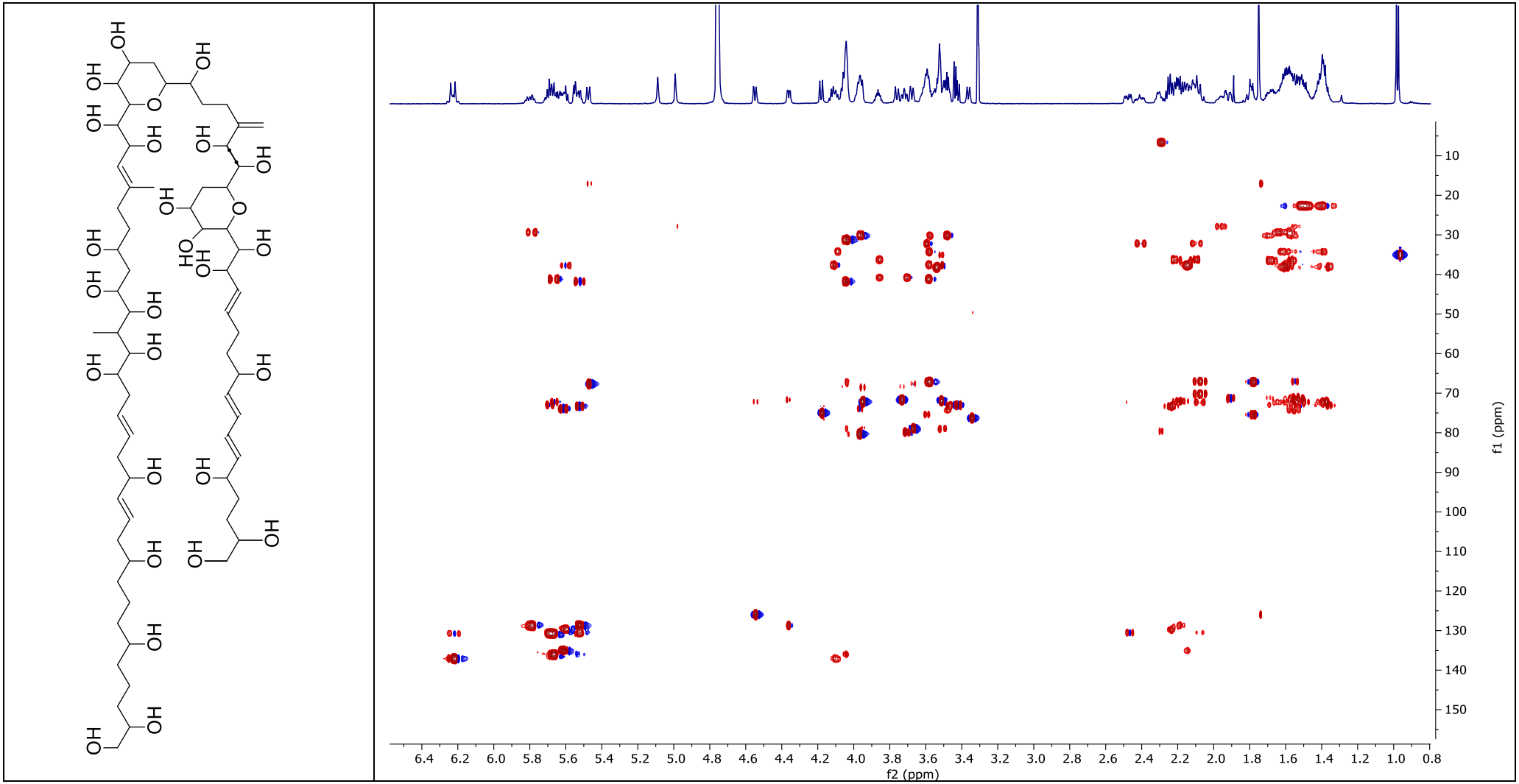


Figure S7. T-ROESY spectrum (600 MHz, CD_3OD) for amphidinol 24.

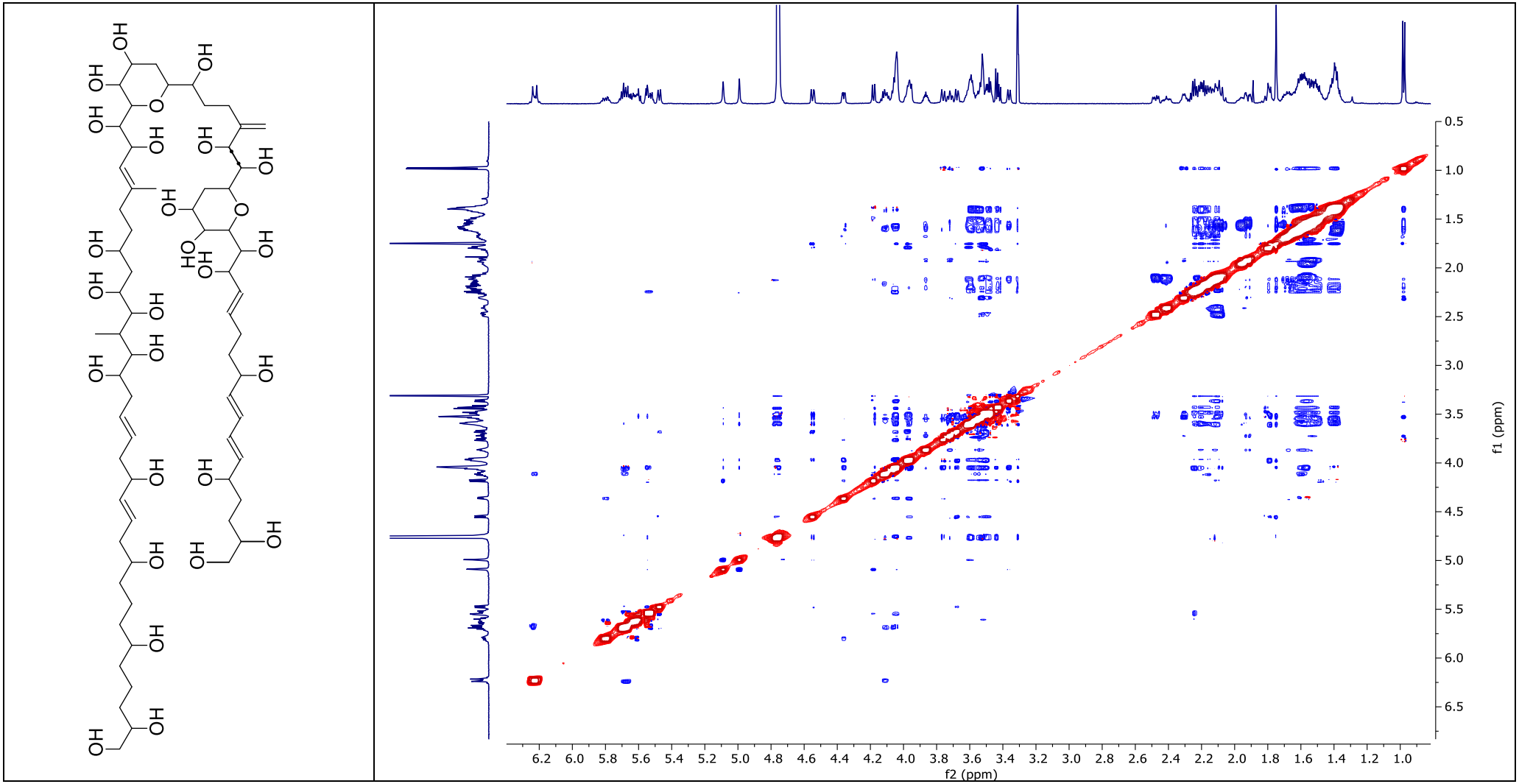


Figure S8. 1D-NOESY spectra (600 MHz, CD_3OD) for amphidinol 24.

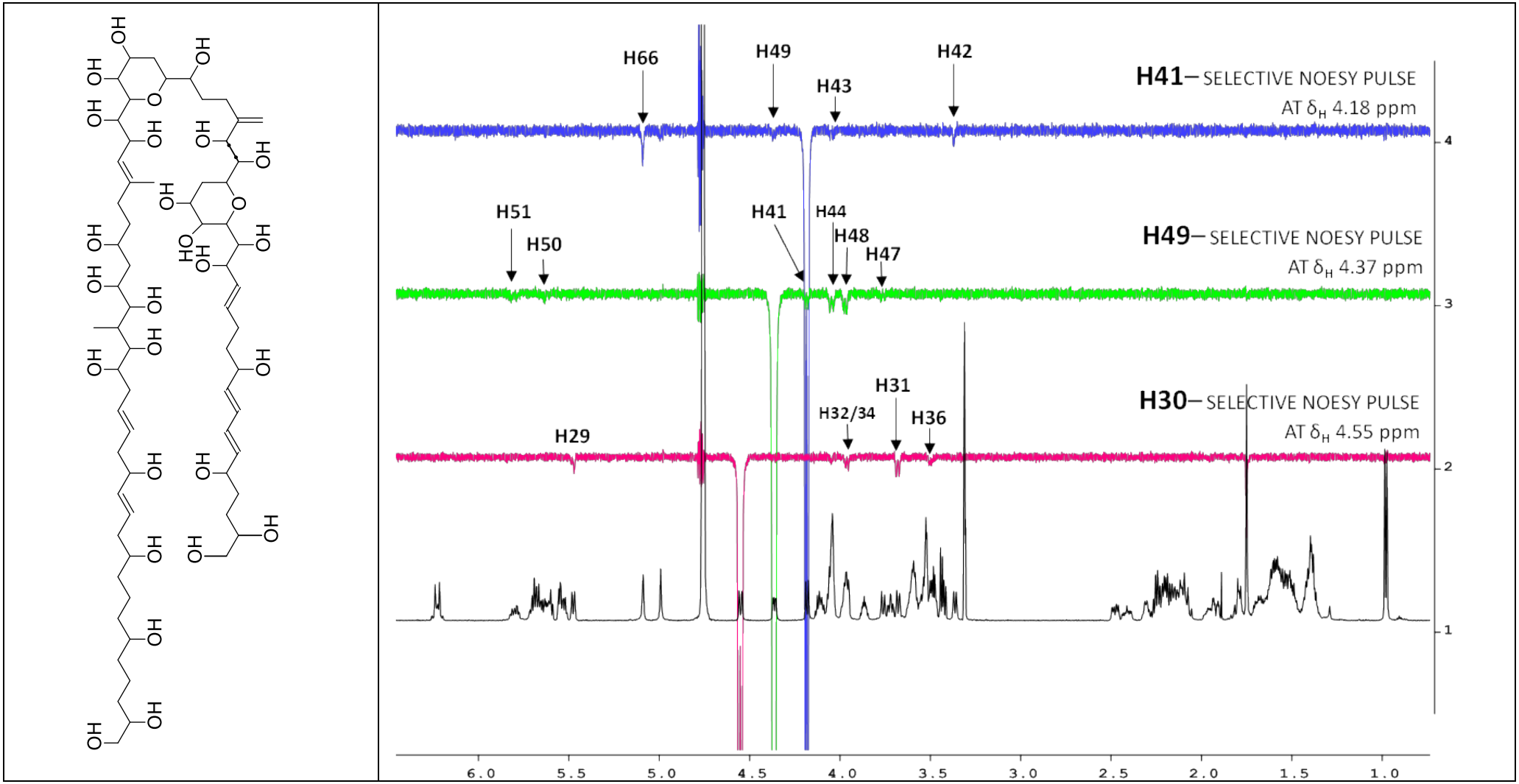


Figure S9. ^{1}H NMR spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

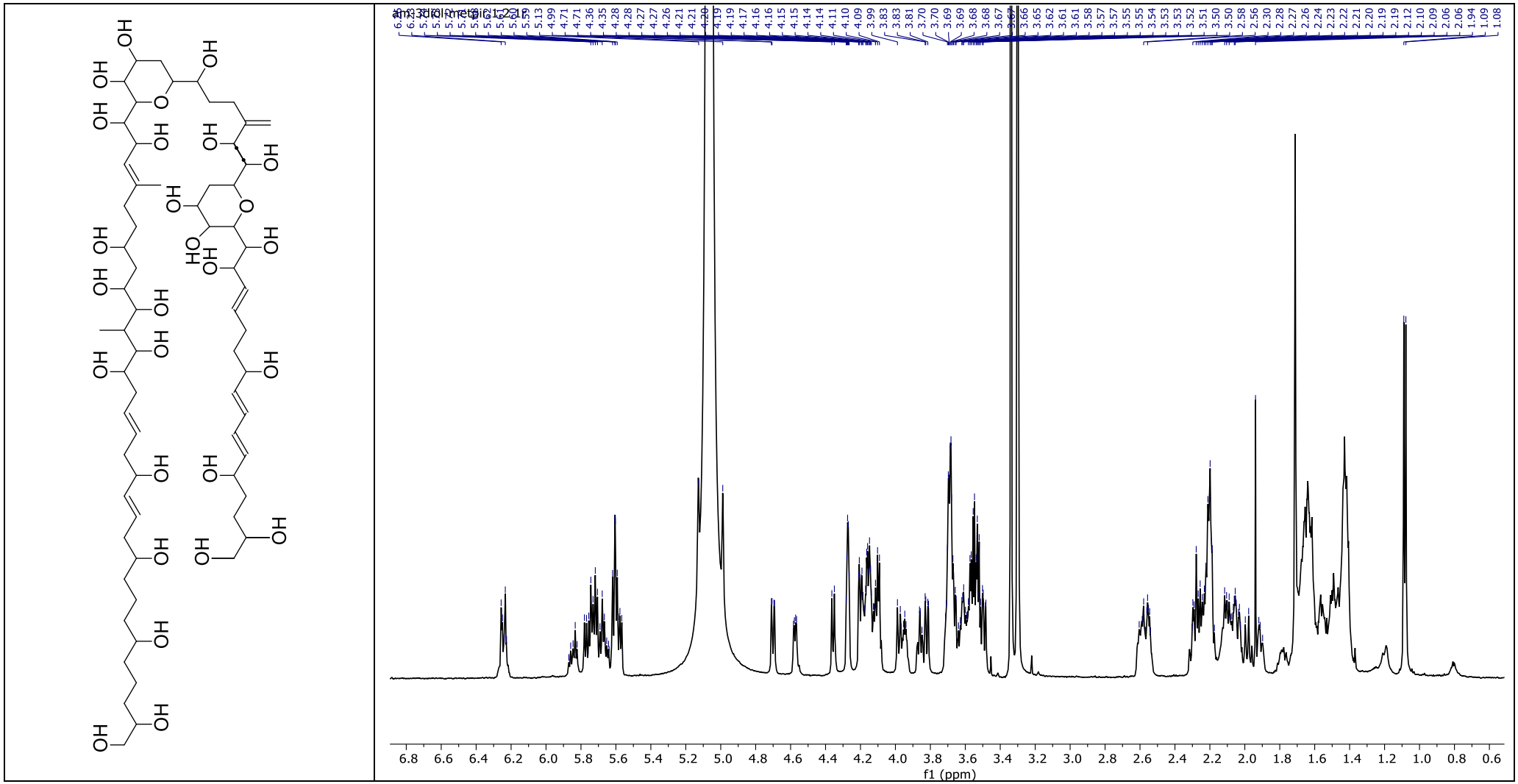


Figure S10. $HSQC_{ed}$ spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

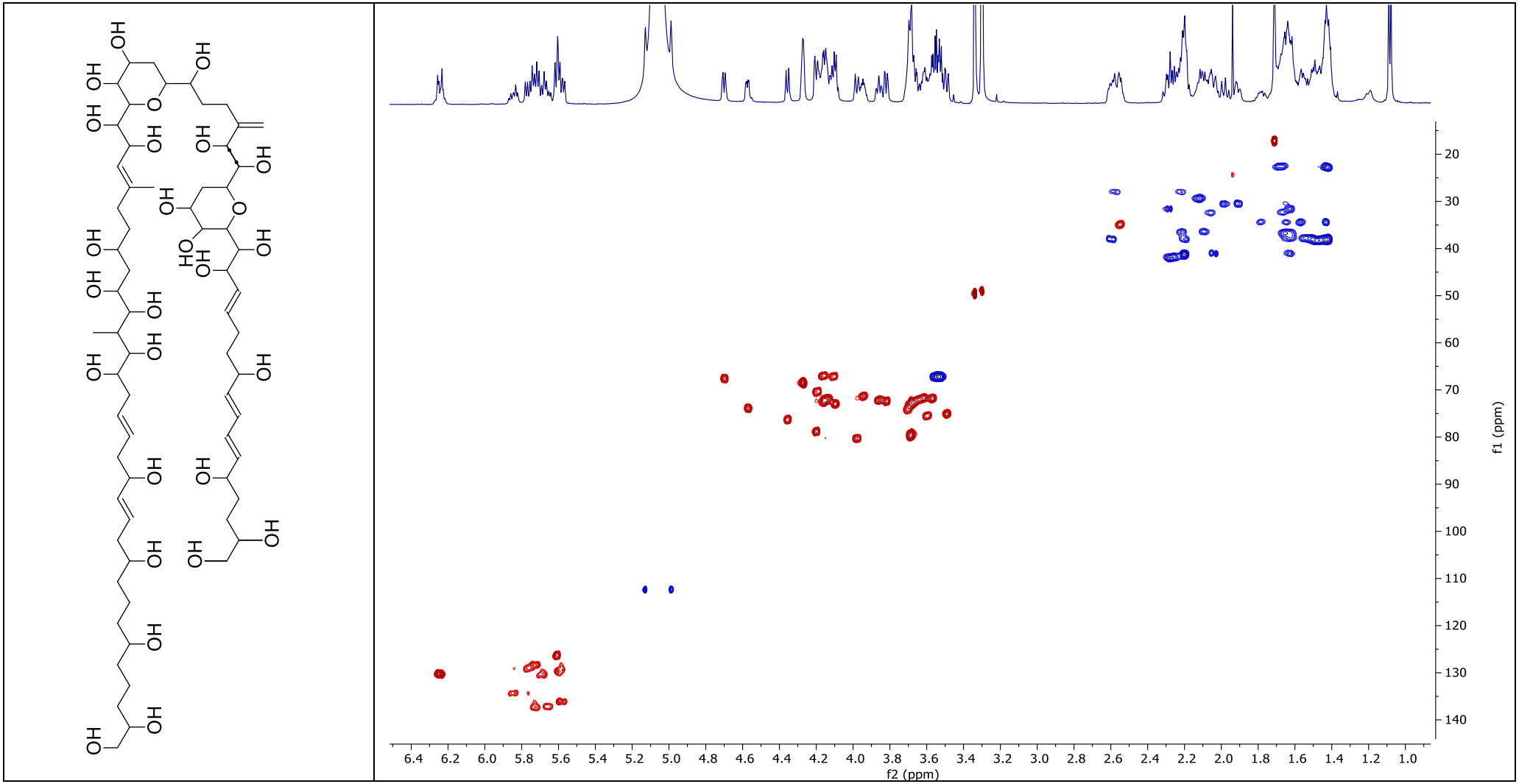


Figure S11. HSQC-TOCSY spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

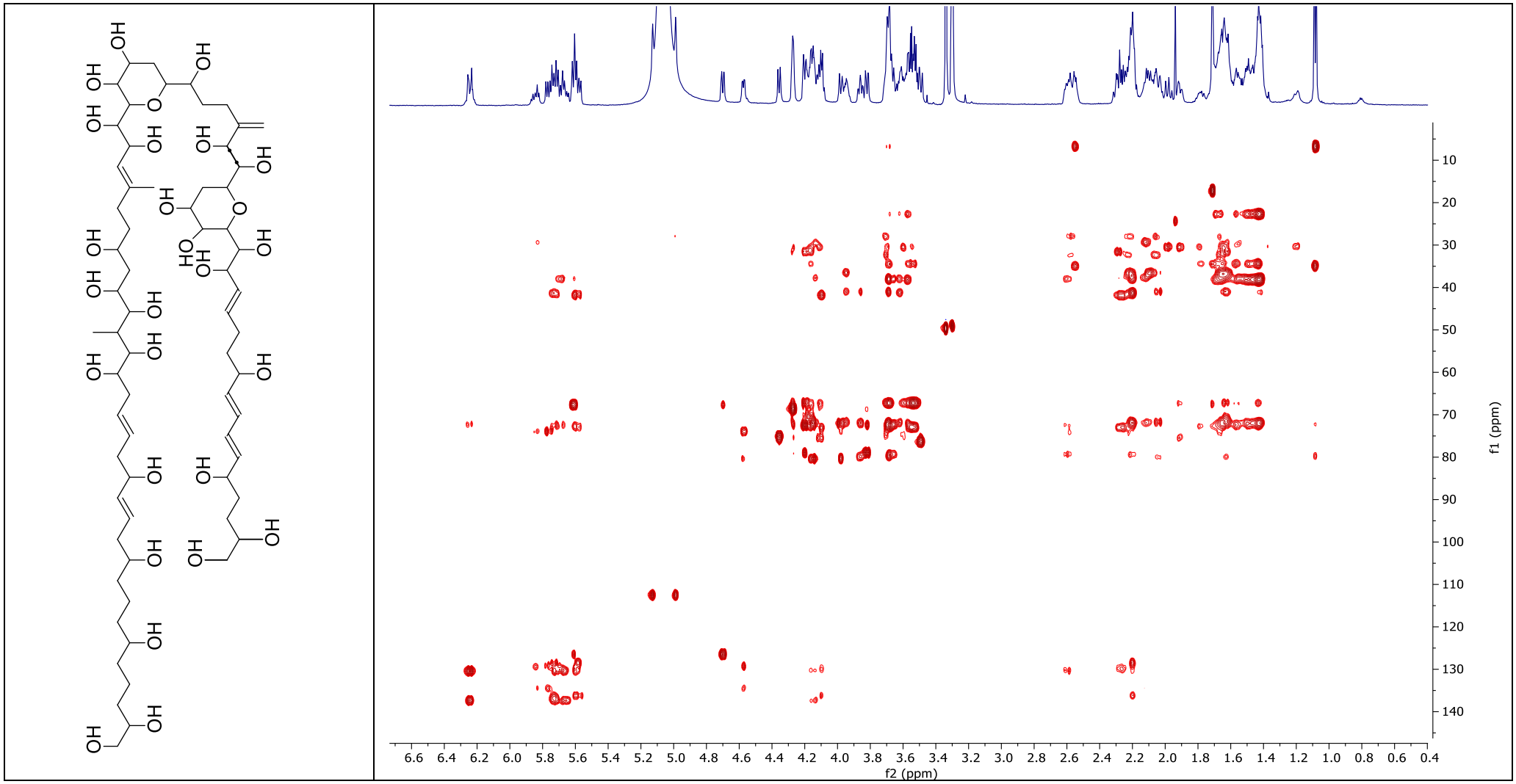


Figure S12. HMBC spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

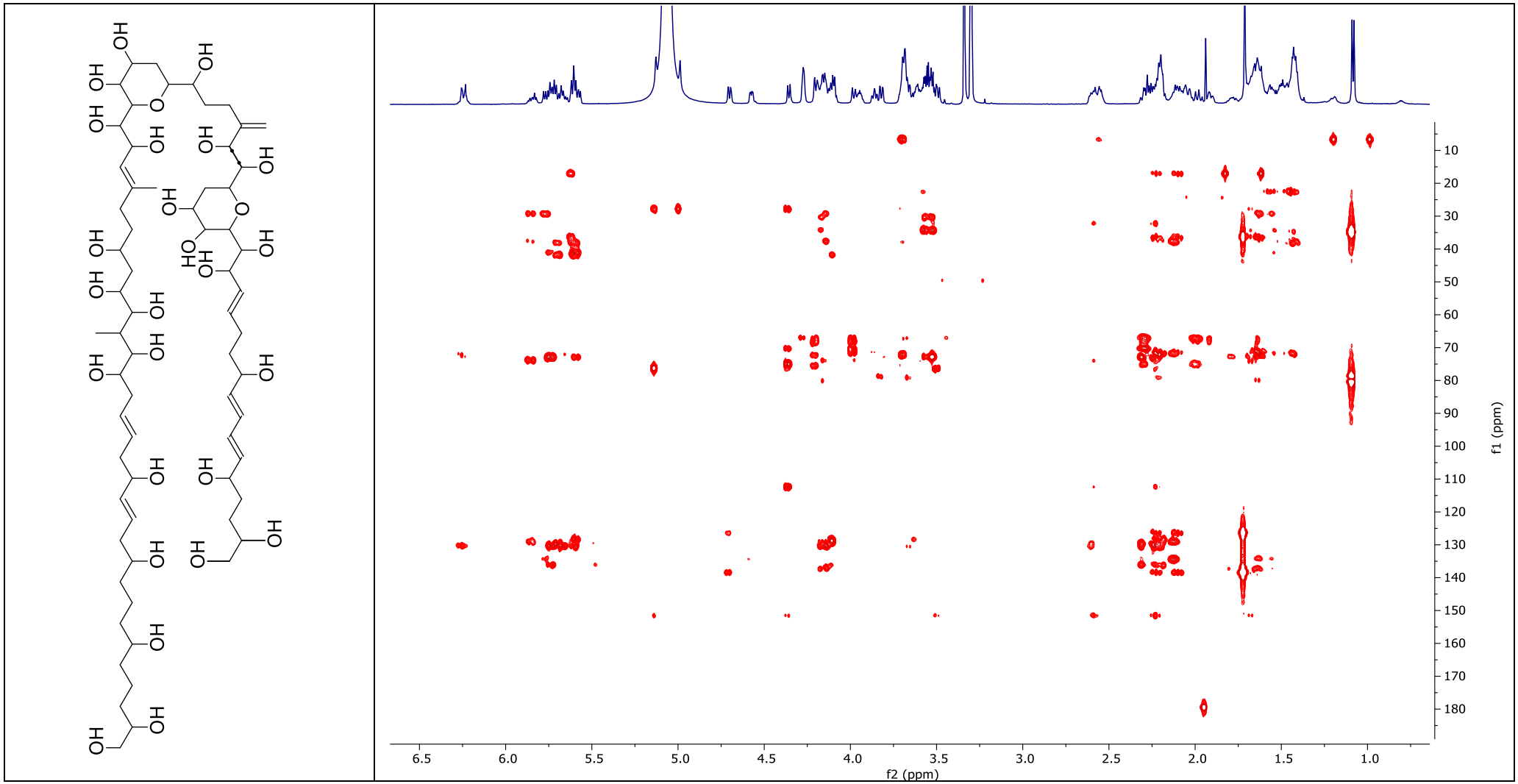


Figure S13. H2BC spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

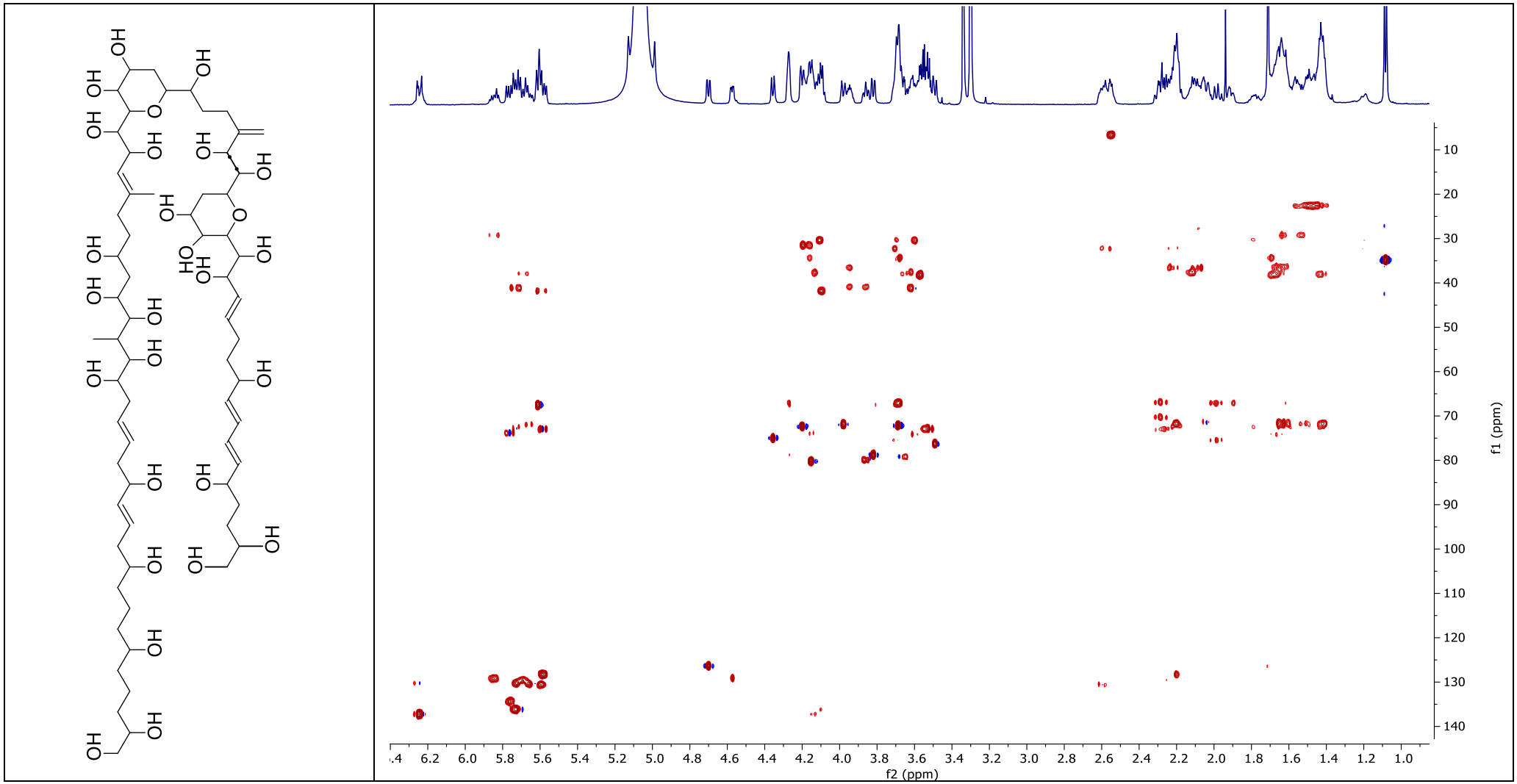


Figure S14. T-ROESY spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

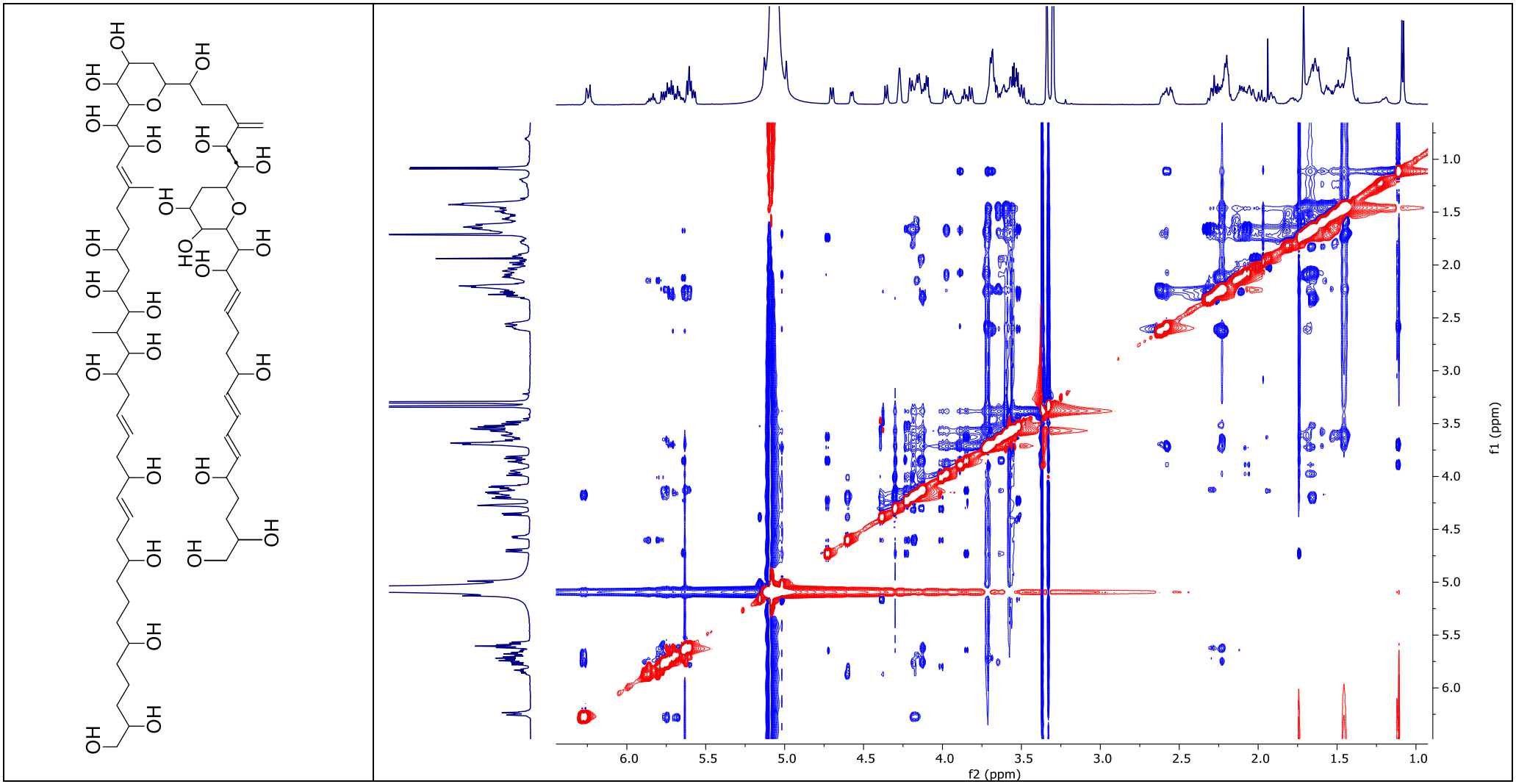


Figure S15. 1D-NOESY spectrum (600 MHz, CD_3OD-C_5D_5N 2:1) for amphidinol 24.

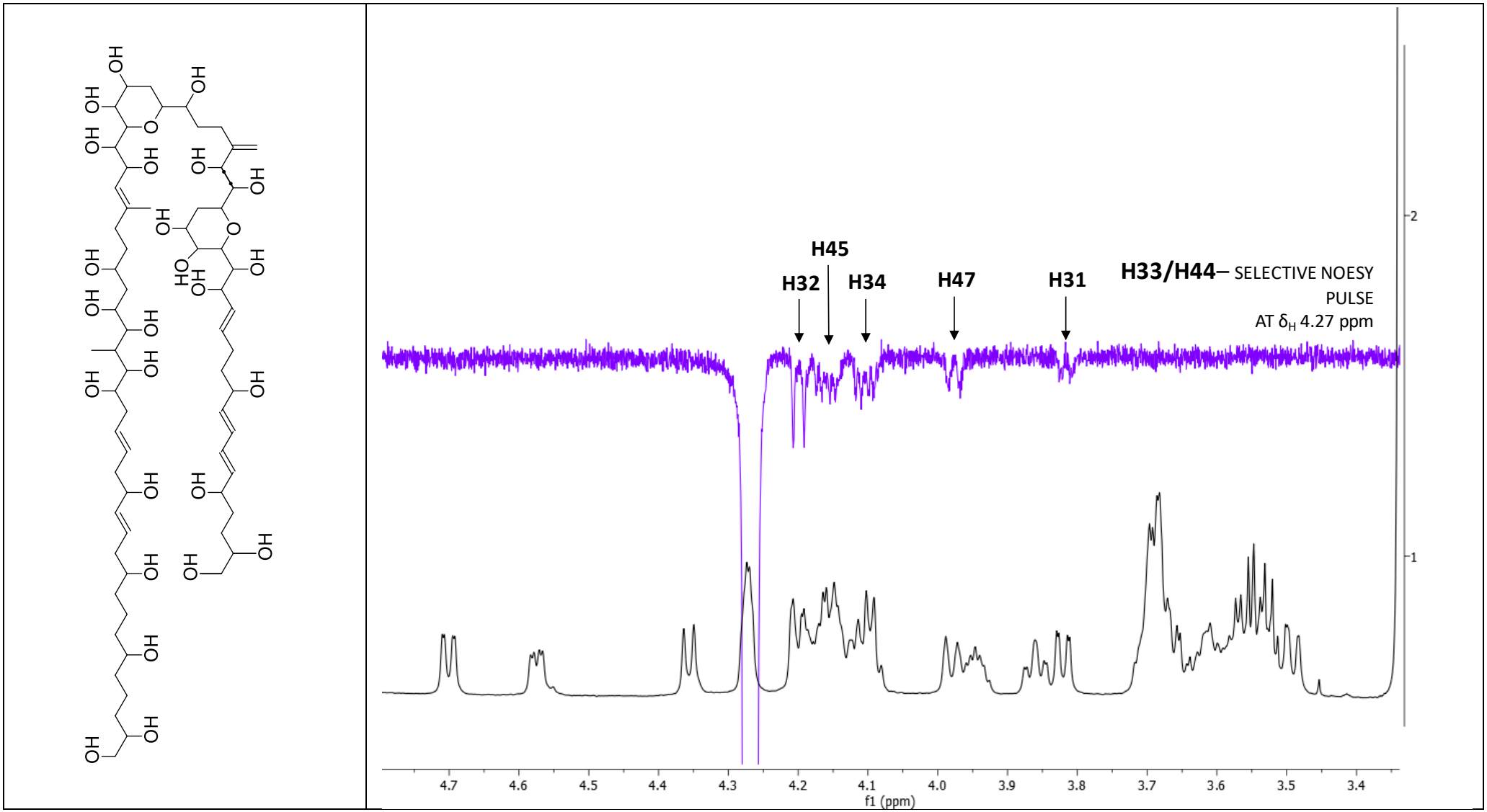
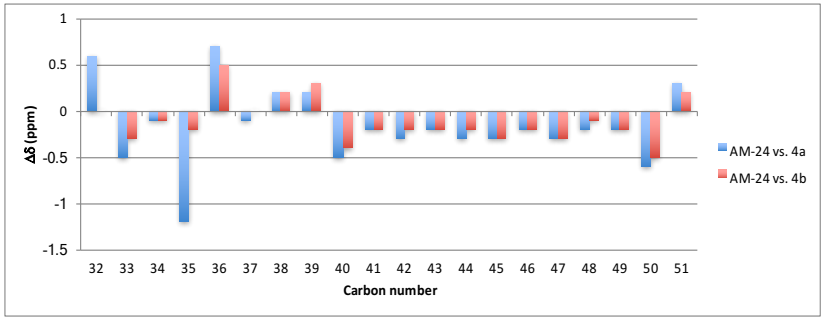
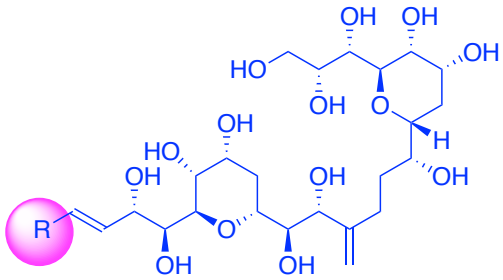


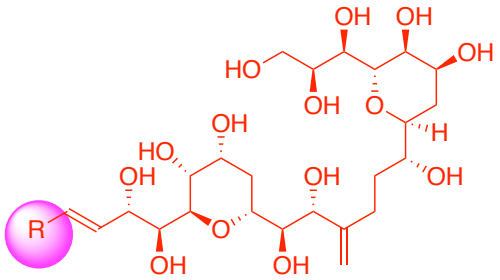
Table S2. ^{1}H and ^{13}C NMR data comparison for carbons C-30 → C-51 in CD_3OD-C_5D_5N 2:1 for amphidinol 24 *versus* related synthetic fragments 4a and 4b reported by Wakamiya et al [22].

#	δC, type					#	δH				
	CD_3OD-C_5D_5N 2:1	4a	am 24 / 4a	4b	am 24 / 4b		CD_3OD-C_5D_5N 2:1	4a	am 24 / 4a	4b	am 24 / 4b
30	67.6, CH	71.1	-3,5	70.9	-3,3	**30**	4.7	4.08	0,62	4.07	0,63
31	72.4, CH	68.3	4,1	67.8	4,6	**31**	3.82	4.14	-0,32	4.15	-0,33
32	78.9, CH	78.3	0,6	78.9	0	**32**	4.2	4.26	-0,06	4.25	-0,05
33	68.6, CH	69.1	-0,5	68.9	-0,3	**33**	4.27	4.33	-0,06	4.36	-0,09
34	67.2, CH	67.3	-0,1	67.3	-0,1	**34**	4.11	4.11	0	4.11	0
35	30.5, CH_2	31.7	-1,2	30.7	-0,2	**35**	1.91	1.69	0,22	1.90	0,01
							1.99	2.08	-0,09	2.02	-0,03
36	75.5, CH	74.8	0,7	75	0,5	**36**	3.6	3.62	-0,02	3.60	0
37	74.1, CH	74.2	-0,1	74.1	0	**37**	3.7	3.65	0,05	3.73	-0,03
38	32.4, CH_2	32.2	0,2	32.2	0,2	**38**	1.67	1.73	-0,06	1.72	-0,05
							2.06	1.91	0,15	1.96	0,1
39	28.0, CH_2	27.8	0,2	27.7	0,3	**39**	2.22	2.24	-0,02	2.24	-0,02
							2.58	2.54	0,04	2.56	0,02
40	151.5, C	152.0	-0,5	151.9	-0,4	**41**	4.36	4.39	-0,03	4.38	-0,02
41	76.3, CH	76.5	-0,2	76.5	-0,2	**42**	3.5	3.51	-0,01	3.50	0
42	75.1, CH	75.4	-0,3	75.3	-0,2	**43**	4.19	4.19	0	4.21	-0,02
43	70.4, CH	70.6	-0,2	70.6	-0,2	**44**	1.63	1.64	-0,01	1.62	0,01
44	31.6, CH_2	31.9	-0,3	31.8	-0,2		2.29	2.34	-0,05	2.33	-0,04
45	67.0, CH	67.3	-0,3	67.3	-0,3	**45**	4.16	4.18	-0,02	4.17	-0,01
46	68.5, CH	68.7	-0,2	68.7	-0,2	**46**	4.28	4.34	-0,06	4.33	-0,05
47	80.3, CH	80.6	-0,3	80.6	-0,3	**47**	3.97	4.02	-0,05	4.00	-0,03
48	72.0, CH	72.2	-0,2	72.1	-0,1	**48**	4.15	4.20	-0,05	4.19	-0,04
49	73.9, CH	74.1	-0,2	74.1	-0,2	**49**	4.57	4.63	-0,06	4.61	-0,04
50	129.2, CH	129.8	-0,6	129.7	-0,5	**50**	5.76	5.78	-0,02	5.76	0
51	134.4, CH	134.1	0,3	134.2	0,2	**51**	5.85	5.81	0,04	5.81	0,04





4a



4b

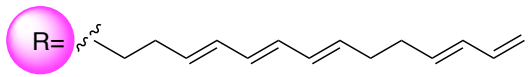


Figure S16. HRESIMS spectrum for amphidinol 24.

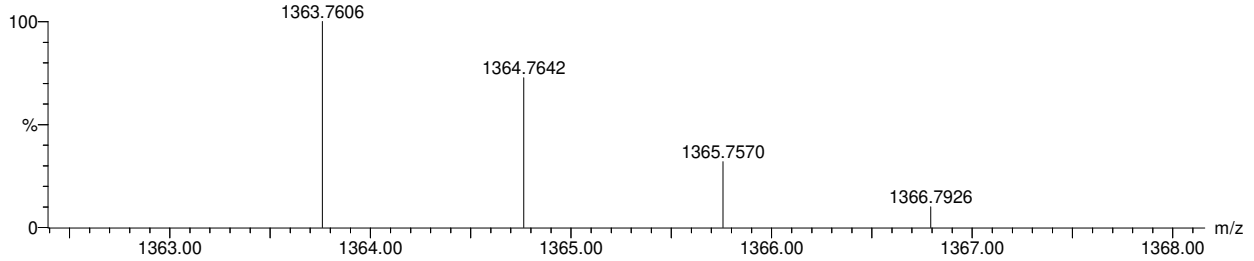
Elemental Composition Report **Page 1**

Multiple Mass Analysis: 3 mass(es) processed
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
303 formula(e) evaluated with 5 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-70 H: 0-120 O: 0-30 Na: 0-1

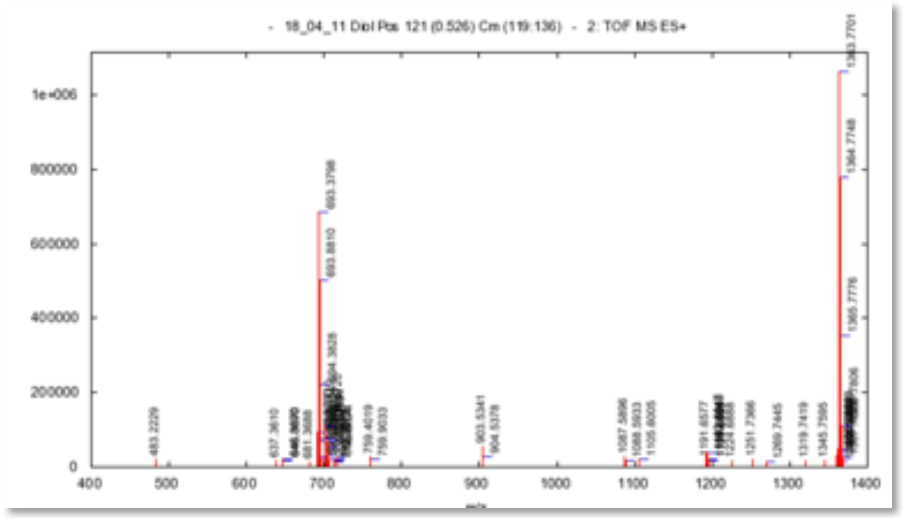
David
(ESI 18-69) Adrian M (AcO 3 Sigma 1 B (F+G) 7) 65 (2.843)

1: TOF MS ES+
1.12e+003



Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
Minimum:	15.00				-1.5			
Maximum:	100.00		5.0	5.0	100.0			
1363.7606	100.00	1363.7602	0.4	0.3	8.5	11.6	0.2	C66 H116 O27 Na
		1363.7626	-2.0	-1.5	11.5	13.0	1.6	C68 H115 O27
1364.7642	72.64	---						
1365.7570	31.81	1365.7630	-6.0	-4.4	6.5	25.5	0.9	C64 H117 O30
		1365.7606	-3.6	-2.6	3.5	25.5	1.0	C62 H118 O30 Na
		1365.7547	2.3	1.7	12.5	26.0	1.5	C69 H114 O25 Na

Figure S17. Main MS/MS fragments observed for amphidinol 24.



ID	*m/z*	Formula	Calc.	Deviation	Losses	Add.	Score	Bonds
1	1251.7366	$C_{63}H_{111}O_{24}$	1251.7465	- 9.9 mDa	- $C_3H_6O_3$	+ 3H	1.5	2
2	1251.7366	$C_{63}H_{111}O_{24}$	1251.7465	- 9.9 mDa	- $C_3H_6O_3$	+ 3H	1.5	2
3	1224.6888	$C_{60}H_{104}O_{24}$	1224.6867	+ 2.1 mDa	- $C_6H_{13}O_2$	+ 2H	2.0	2
4	1193.6669	$C_{59}H_{101}O_{24}$	1193.6683	- 1.4 mDa	- $C_7H_{16}O_3$	+ 0H	5.0	2
5	1193.6669	$C_{59}H_{101}O_{24}$	1193.6683	- 1.4 mDa	- $C_7H_{16}O_3$	+ 0H	5.0	2
6	759.4019	$C_{34}H_{63}O_{18}$	759.4019	+ 0.5 mDa	- $C_{32}H_{54}O_9$	+ 3H	2.0	2
7	705.3731	$C_{34}H_{57}O_{15}$	705.3731	+ 3.4 mDa	- $C_{32}H_{60}O_{12}$	+ 1H	1.5	2
8	702.3754	$C_{35}H_{58}O_{18}$	702.3754	- 7.3 mDa	- $C_{32}H_{59}O_{13}$	- 2H	2.0	2
9	701.3720	$C_{35}H_{57}O_{14}$	701.3720	- 2.8mDa	- $C_{31}H_{60}O_{13}$	+ 1H	2.0	2
10	695.3849	$C_{33}H_{58}O_{15}$	695.3849	- 0.5 mDa	- $C_{33}H_{58}O_{12}$	+ 3H	2.0	2
11	694.3828	$C_{35}H_{58}O_{15}$	694.3828	+ 5.2 mDa	- $C_{33}H_{59}O_{12}$	+ 2H	2.0	2
12	681.3688	$C_{32}H_{57}O_{15}$	681.3697	- 0.9 mDa	- $C_{34}H_{60}O_{12}$	+ 3H	2.0	2

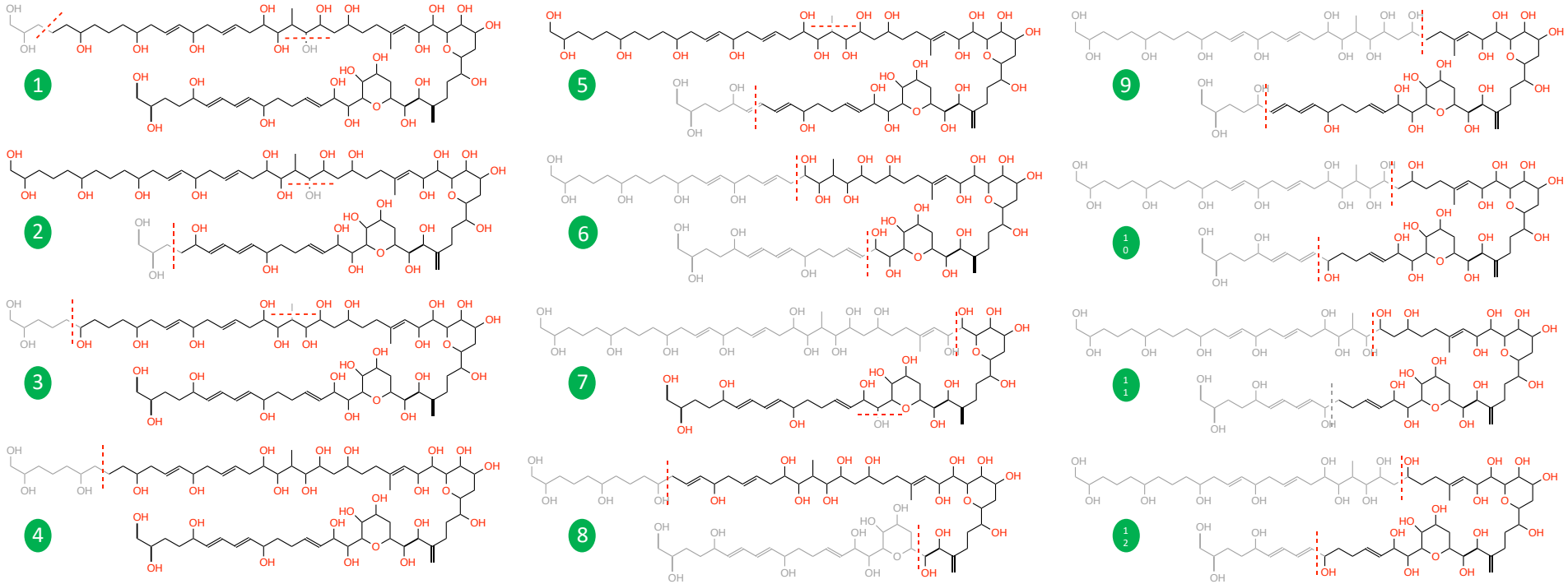


Figure S18. ^{1}H NMR spectrum (600 MHz, CD_3OD) for amphidinol 25.

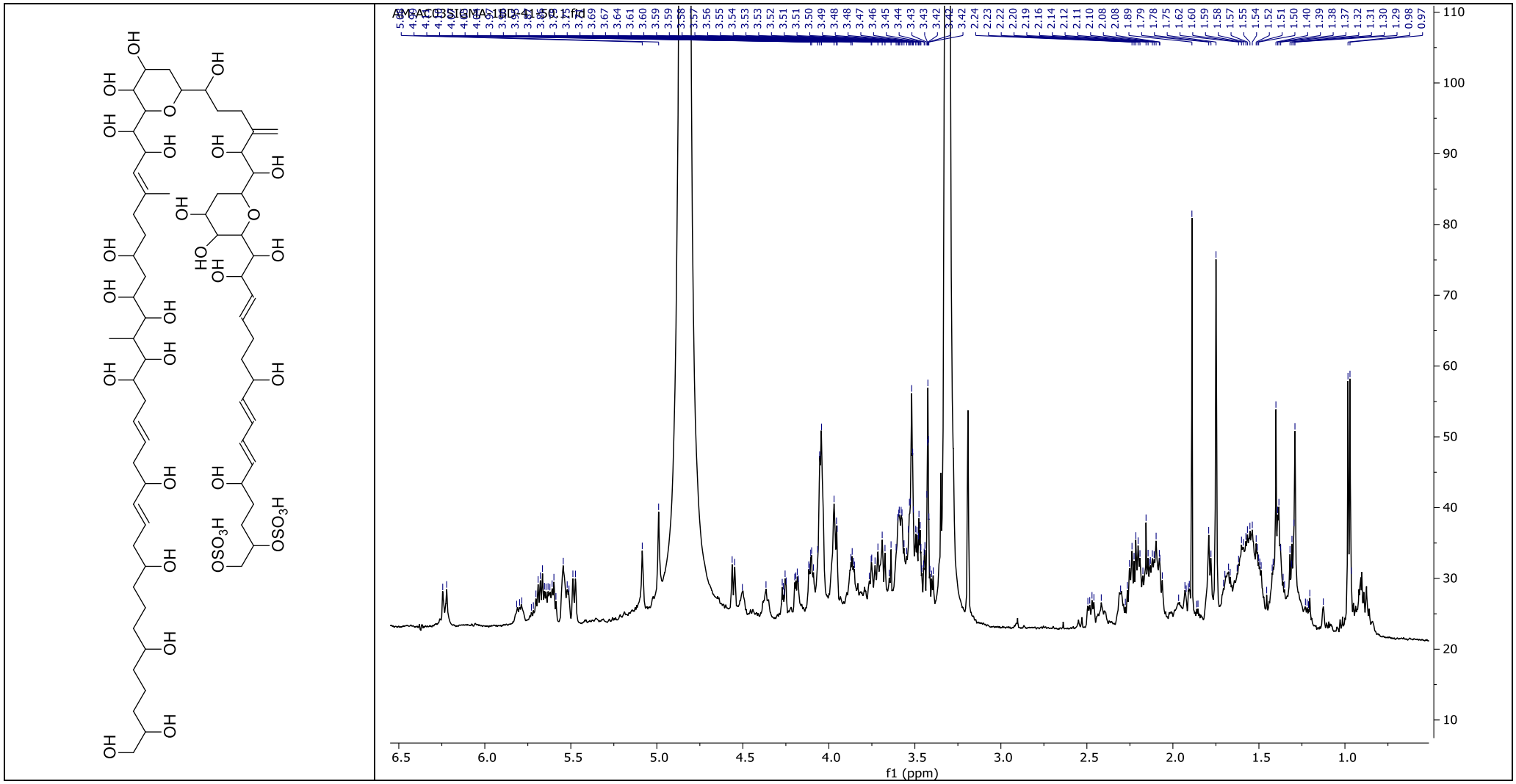


Figure S19. COSY spectrum (600 MHz, CD_3OD) for amphidinol 25.

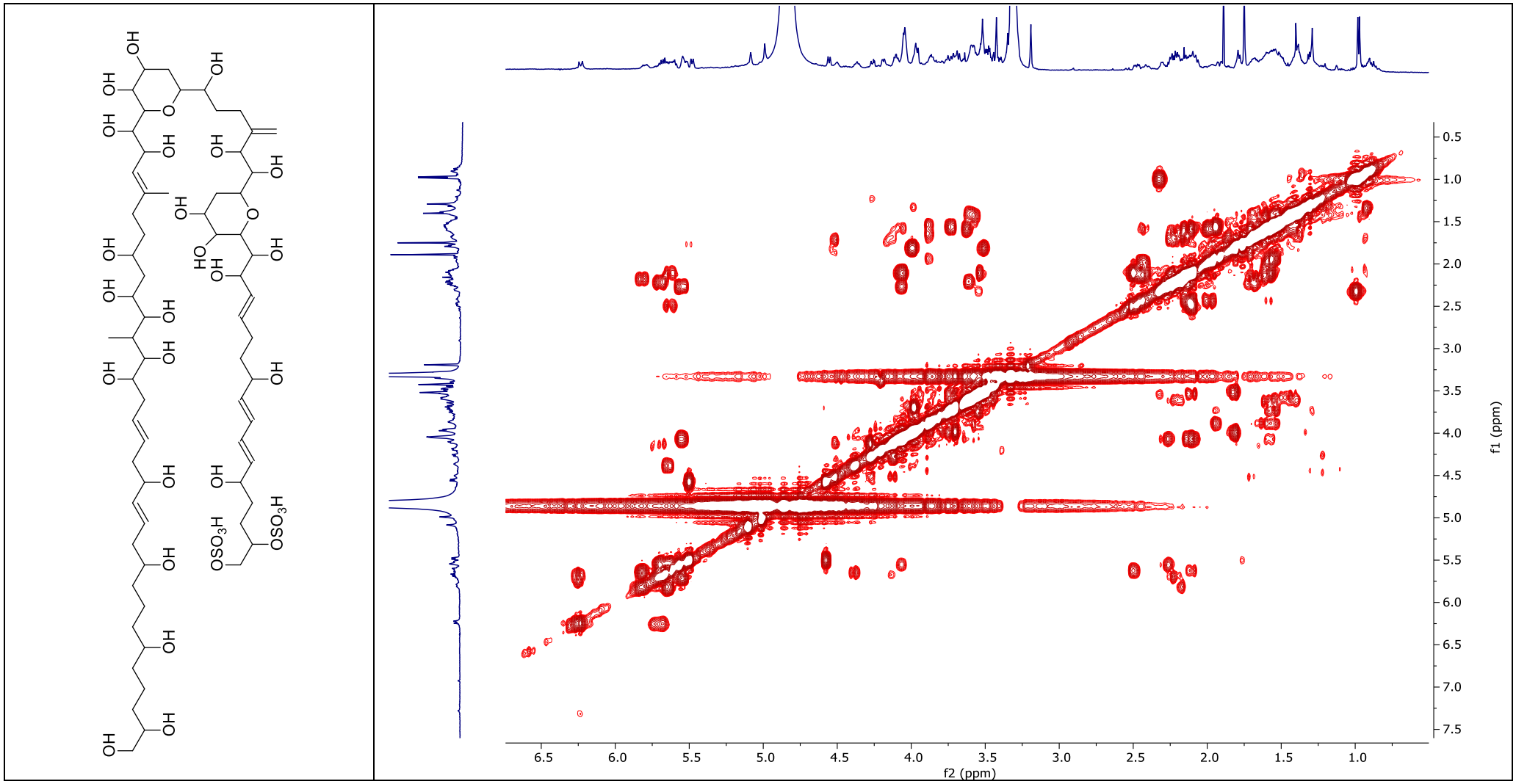


Figure S20. $HSQC_{ed}$ spectrum (600 MHz, CD_3OD) for amphidinol 25.

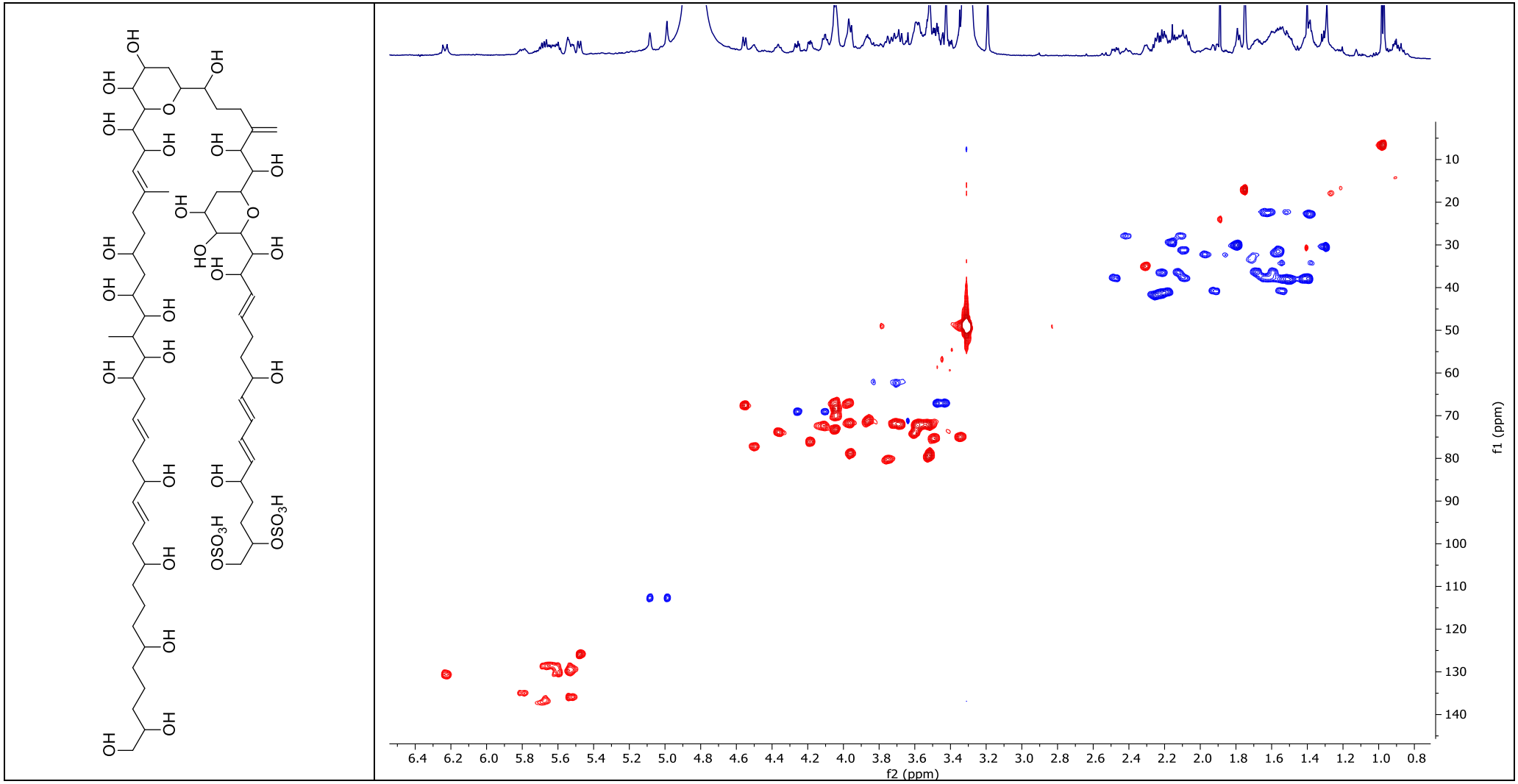


Figure S21. HSQC-TOCSY spectrum (600 MHz, CD_3OD) for amphidinol 25.

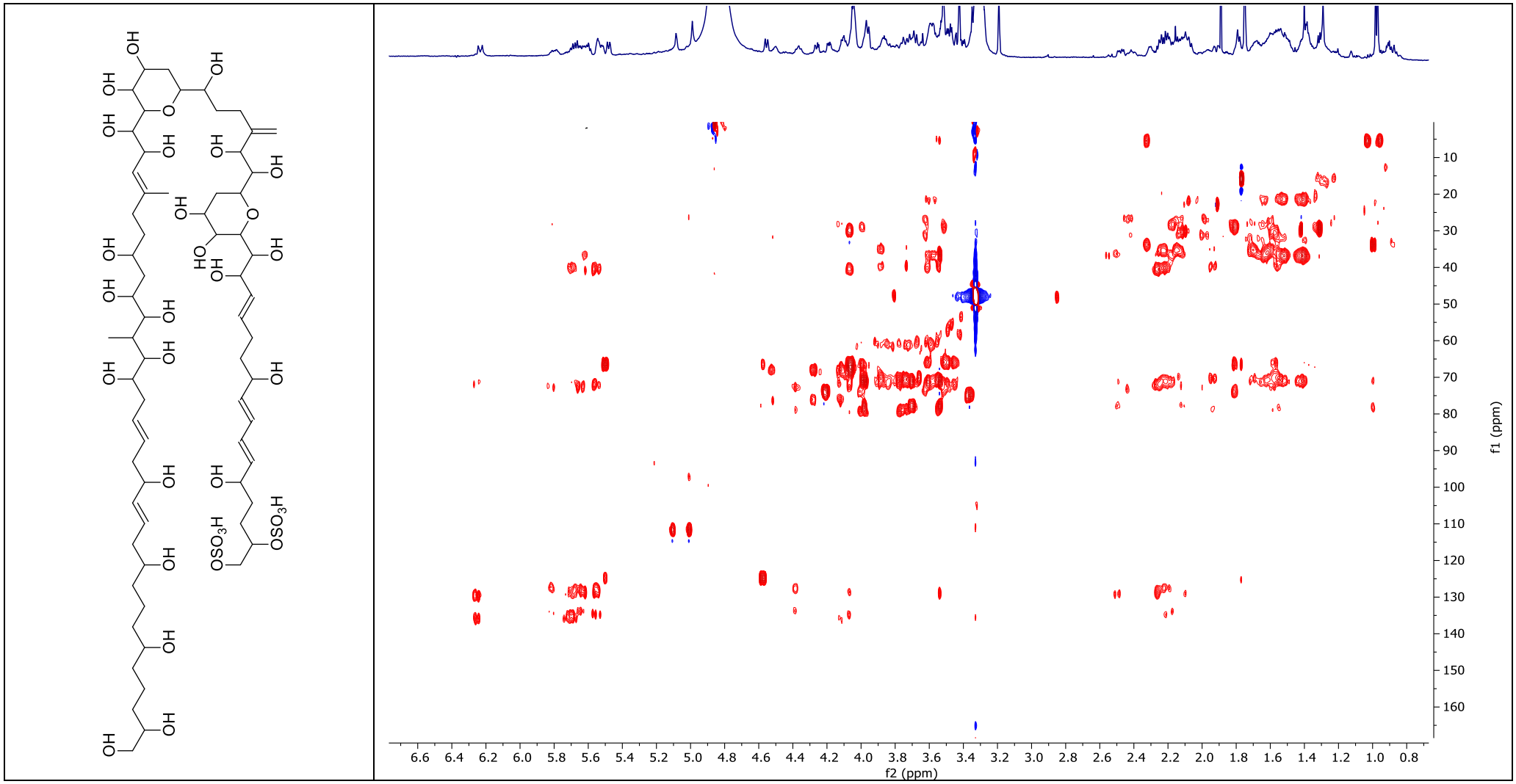


Figure S22. HMBC spectrum (600 MHz, CD_3OD) for amphidinol 25.

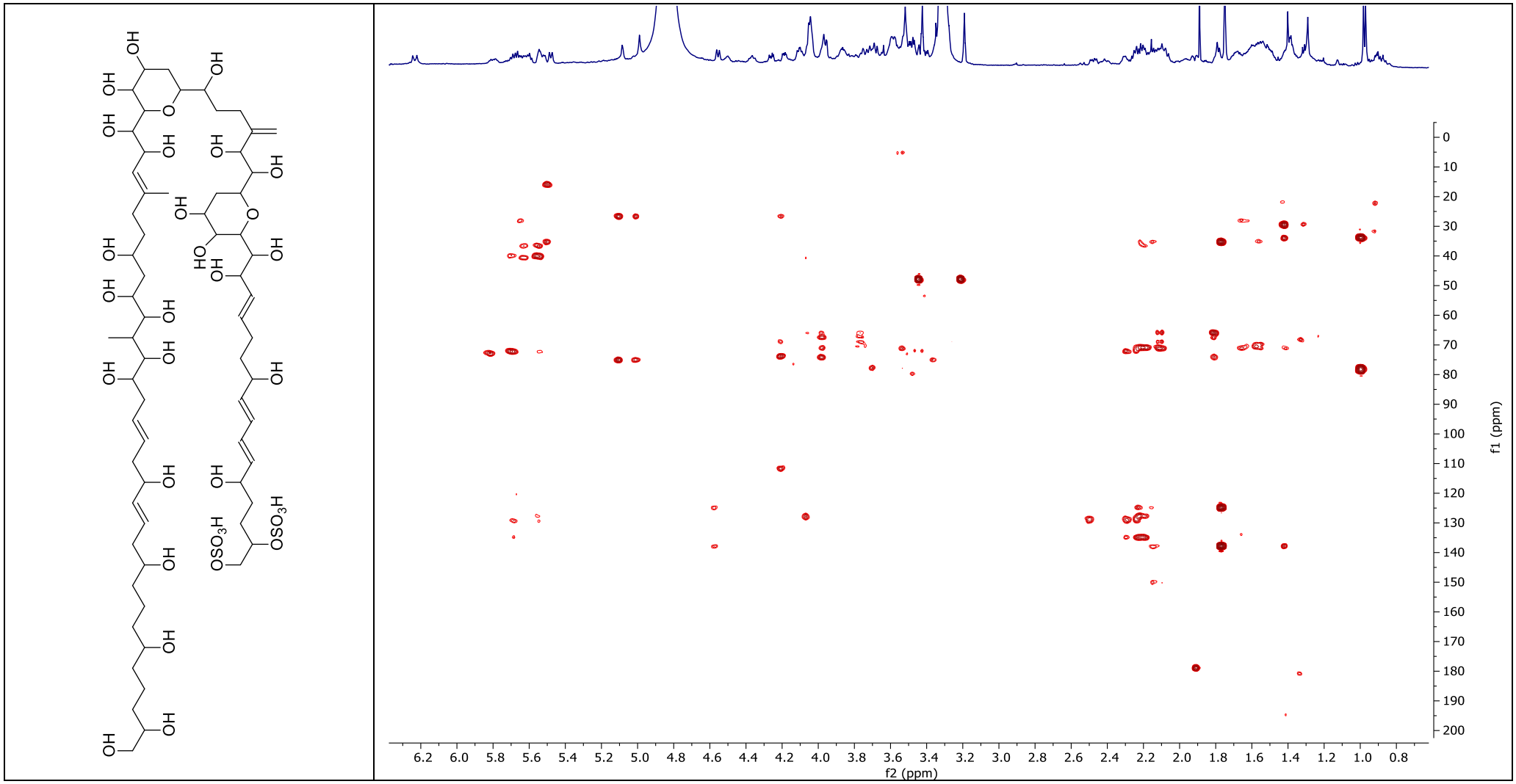
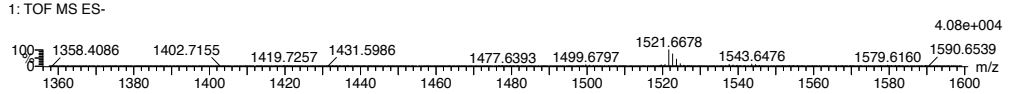


Figure S23. HRESIMS spectrum for amphidinol 25

Elemental Composition Report **Page 1**

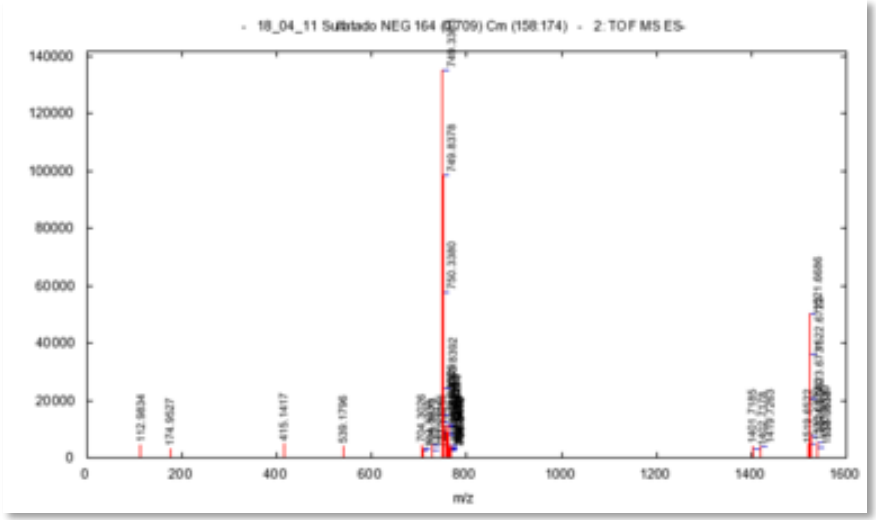
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -50.0, max = 75.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
1111 formula(e) evaluated with 31 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 5-80 H: 0-150 O: 0-40 Na: 0-1 S: 0-2
18_04_11 Sulfatado NEG 161 (0.694) Cm (159:177)
1: TOF MS ES-



Minimum:				-50.0				
Maximum:		40.0	10.0	75.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1521.6678	1521.6819	-14.1	-9.3	27.5	409.5	9.702	0.01	C80 H106 O27 Na
	1521.6642	3.6	2.4	27.5	407.7	7.829	0.04	C80 H106 O25 Na S
	1521.6699	-2.1	-1.4	25.5	408.6	8.750	0.02	C79 H109 O25 S2
	1521.6691	-1.3	-0.9	26.5	406.2	6.395	0.17	C78 H105 O30
	1521.6675	0.3	0.2	22.5	408.0	8.184	0.03	C77 H110 O25 Na S2
	1521.6667	1.1	0.7	23.5	406.0	6.141	0.22	C76 H106 O30 Na
	1521.6724	-4.6	-3.0	21.5	406.2	6.364	0.17	C75 H109 O30 S
	1521.6547	13.1	8.6	21.5	409.7	9.834	0.01	C75 H109 O28 S2
	1521.6538	14.0	9.2	22.5	408.7	8.831	0.01	C74 H105 O33
	1521.6700	-2.2	-1.4	18.5	405.2	5.362	0.47	C73 H110 O30 Na S
	1521.6758	-8.0	-5.3	16.5	407.1	7.260	0.07	C72 H113 O30 S2
	1521.6572	10.6	7.0	17.5	406.2	6.323	0.18	C71 H109 O33 S
	1521.6749	-7.1	-4.7	17.5	406.5	6.659	0.13	C71 H109 O35
	1521.6734	-5.6	-3.7	13.5	405.5	5.700	0.33	C70 H114 O30 Na S2
	1521.6725	-4.7	-3.1	14.5	406.3	6.487	0.15	C69 H110 O35 Na
	1521.6548	13.0	8.5	14.5	406.3	6.431	0.16	C69 H110 O33 Na S
	1521.6783	-10.5	-6.9	12.5	404.9	5.111	0.60	C68 H113 O35 S
	1521.6606	7.2	4.7	12.5	404.7	4.849	0.78	C68 H113 O33 S2
	1521.6597	8.1	5.3	13.5	407.4	7.617	0.05	C67 H109 O38
	1521.6759	-8.1	-5.3	9.5	405.2	5.321	0.49	C66 H114 O35 Na S
	1521.6581	9.7	6.4	9.5	401.6	1.726	17.79	C66 H114 O33 Na S2
	1521.6817	-13.9	-9.1	7.5	400.4	0.536	58.49	C65 H117 O35 S2
	1521.6573	10.5	6.9	10.5	408.7	8.904	0.01	C65 H110 O38 Na
	1521.6808	-13.0	-8.5	8.5	409.3	9.488	0.01	C64 H113 O40
	1521.6631	4.7	3.1	8.5	405.3	5.496	0.41	C64 H113 O38 S
	1521.6793	-11.5	-7.6	4.5	401.6	1.780	16.87	C63 H118 O35 Na S2
	1521.6784	-10.6	-7.0	5.5	409.3	9.471	0.01	C62 H114 O40 Na
	1521.6606	7.2	4.7	5.5	407.0	7.193	0.08	C62 H114 O38 Na S
	1521.6664	1.4	0.9	3.5	403.7	3.880	2.07	C61 H117 O38 S2
	1521.6640	3.8	2.5	0.5	406.2	6.359	0.17	C59 H118 O38 Na S2
	1521.6818	-14.0	-9.2	0.5	409.4	9.595	0.01	C59 H118 O40 Na S

Figure S24. Main MS/MS fragments observed for amphidinol 25.



ID	*m/z*	Formula	Calc.	Deviation	Losses	Add.	Score	Bonds
1	1419.7263	$C_{66}H_{115}O_{30}S$	1419.7194	+ 6.9 mDa	- O_3S	+ 2H	1.0	1
2	1402.7178	$C_{66}H_{114}O_{29}S$	1402.7166	+ 1.2 mDa	- HO_4S	+ 1H	0.5	1
3	1402.7178	$C_{66}H_{114}O_{29}S$	1402.7166	+ 1.2 mDa	- HO_4S	+ 1H	0.5	1
4	1401.7185	$C_{66}H_{113}O_{29}S$	1401.7088	+ 9.7 mDa	- H_2O_4S	+ 0H	0.5	1
5	709.3573	$C_{33}H_{57}O_{16}$	709.3647	- 7.4 mDa	- $C_{33}H_{58}O_{17}S_2$	+ 3H	2.0	2
6	709.3573	$C_{33}H_{58}O_{16}$	709.3647	- 7.4 mDa	- $C_{33}H_{58}O_{17}S_2$	+ 1H	2.0	2
7	539.1706	$C_{22}H_{35}O_{13}S$	539.1798	- 0.2 mDa	- $C_{44}H_{80}O_{20}S$	+ 1H	2.0	2
8	539.1706	$C_{22}H_{35}O_{13}S$	539.1798	- 0.2 mDa	- $C_{44}H_{80}O_{20}S$	+ 1H	2.0	2

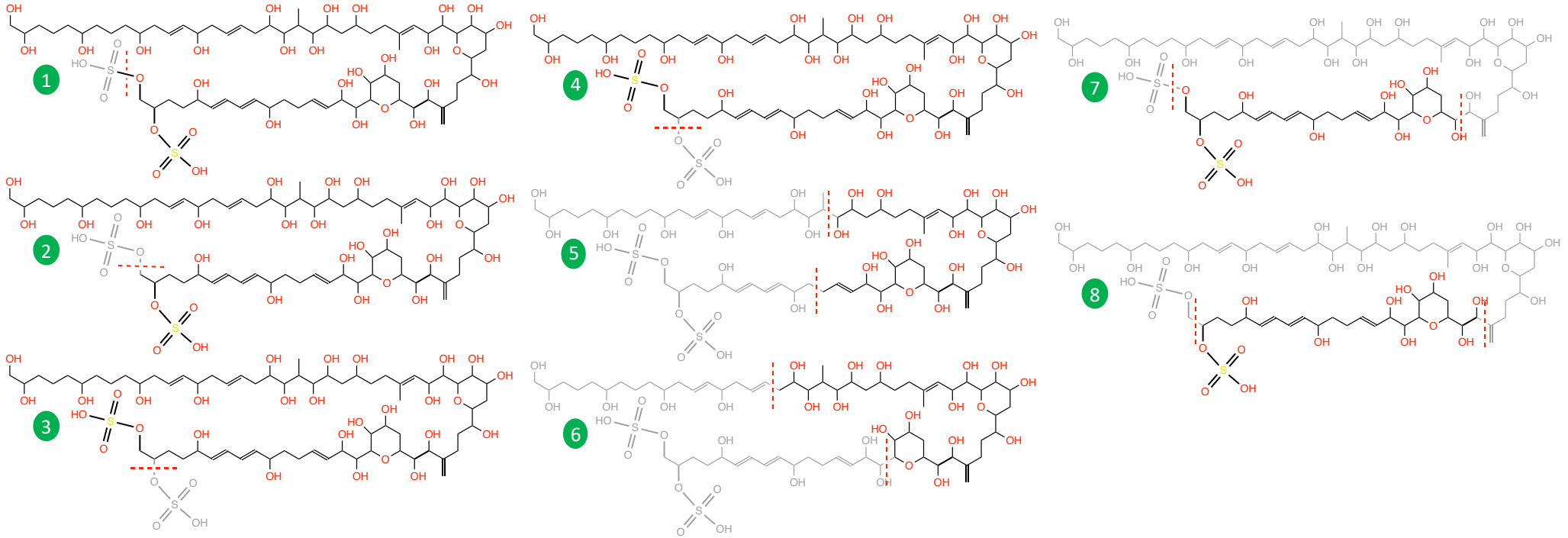


Figure S25. ^{1}H NMR spectrum (600 MHz, CD_3OD) for amphidinol 26.

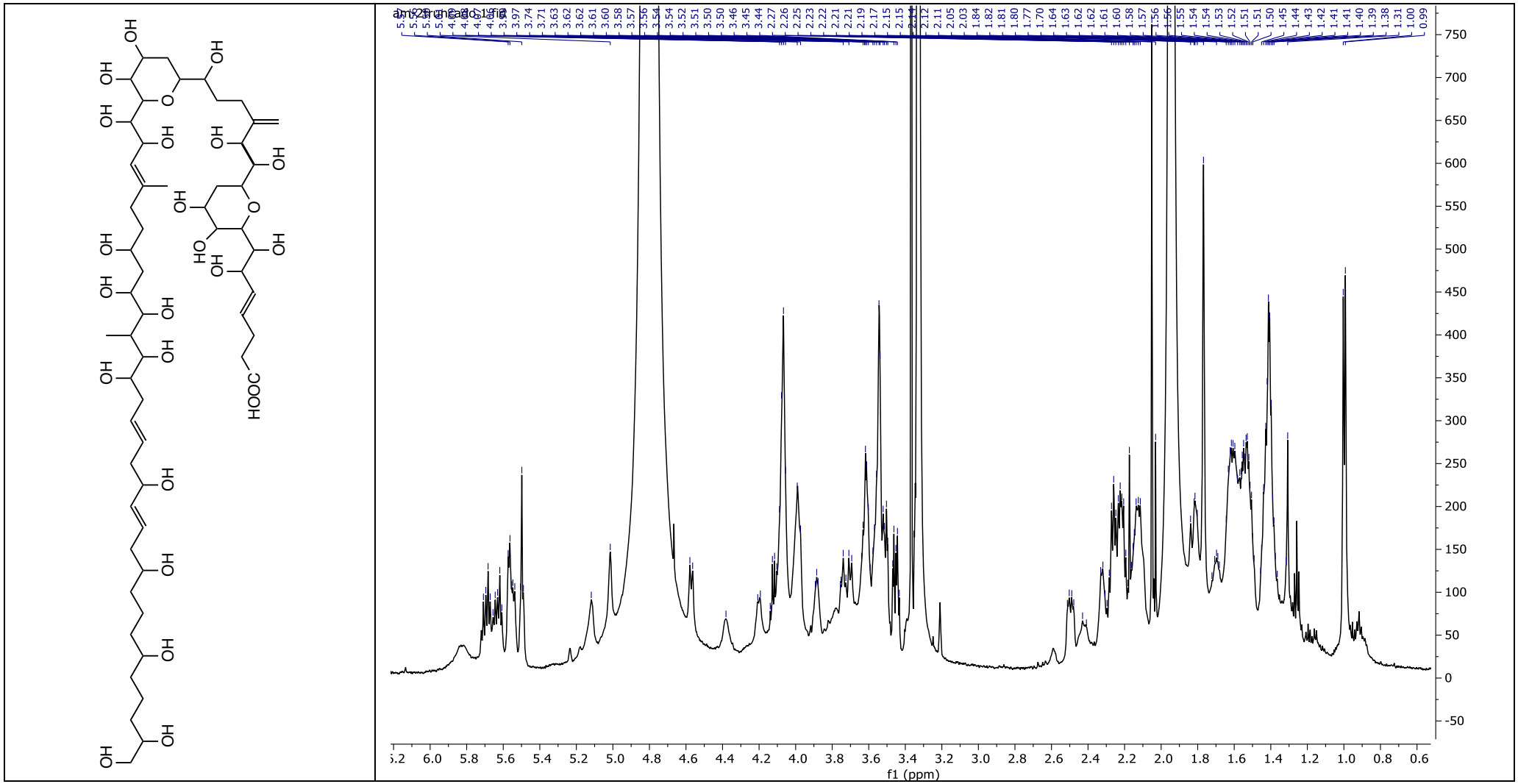


Figure S26. COSY spectrum (600 MHz, CD_3OD) for amphidinol 26.

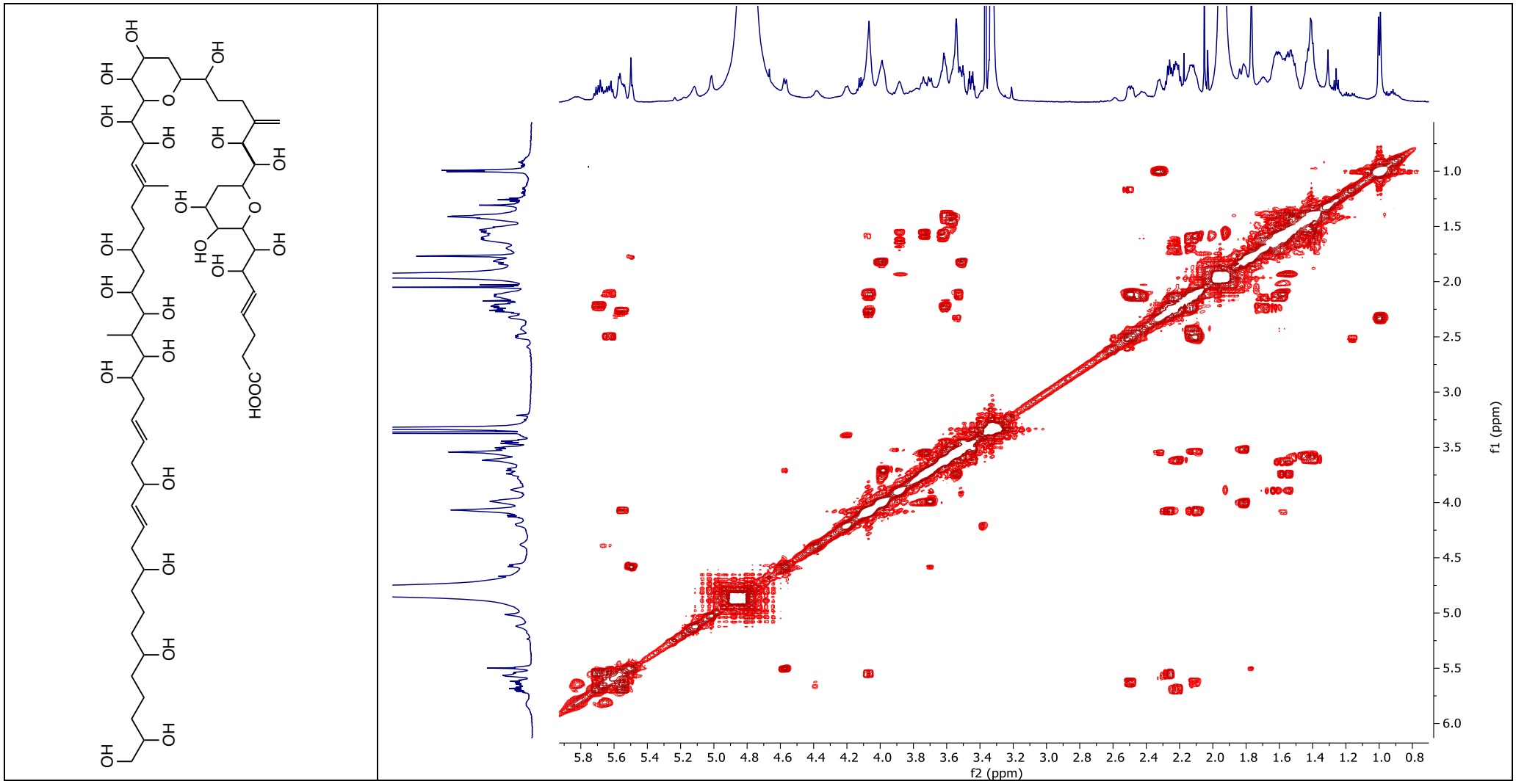


Figure S27. HSQC$_{ed}$ spectrum (600 MHz, CD_3OD) for amphidinol 26.

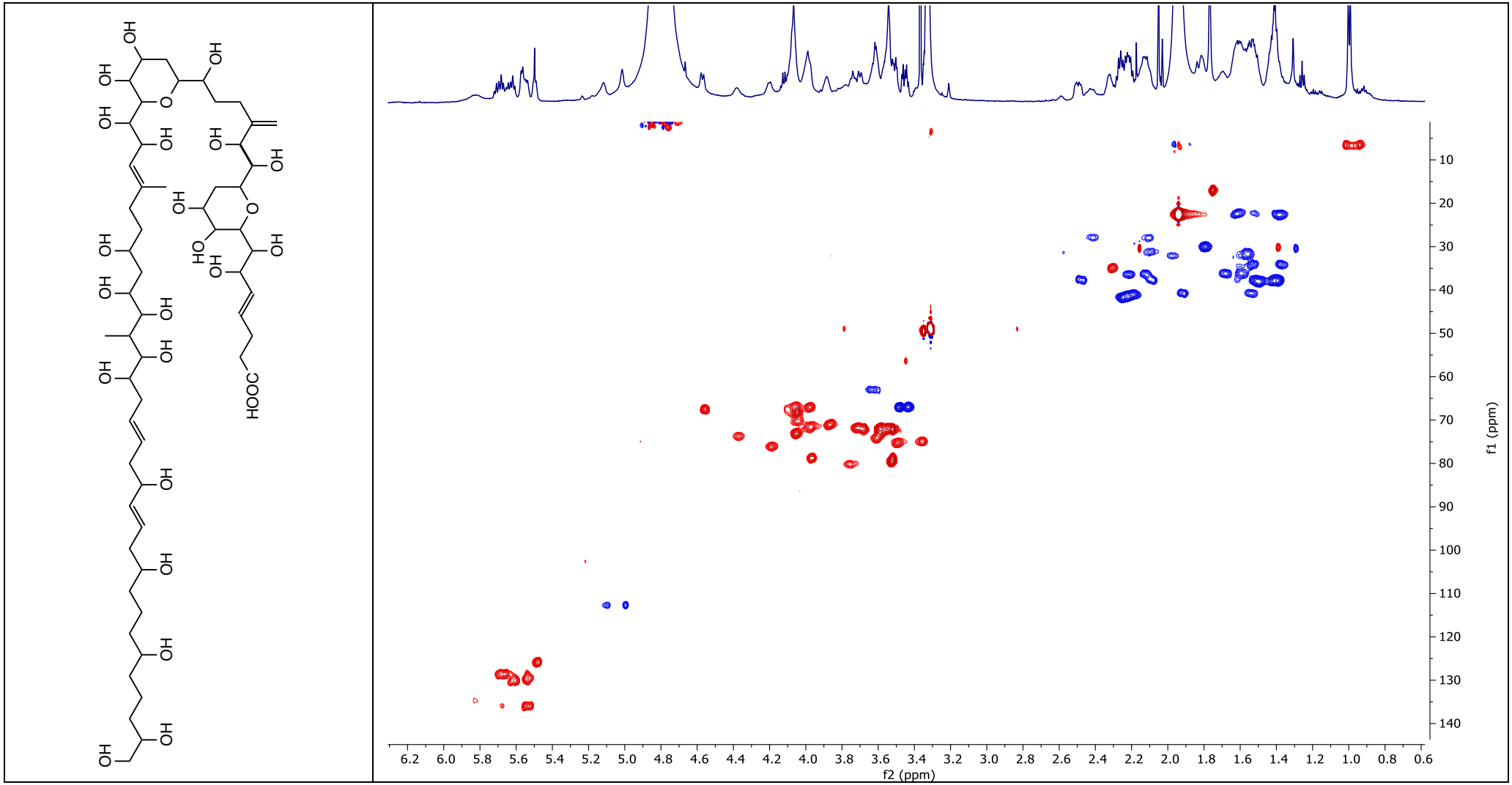


Figure S28. HSQC-TOCSY spectrum (600 MHz, CD_3OD) for amphidinol 26.

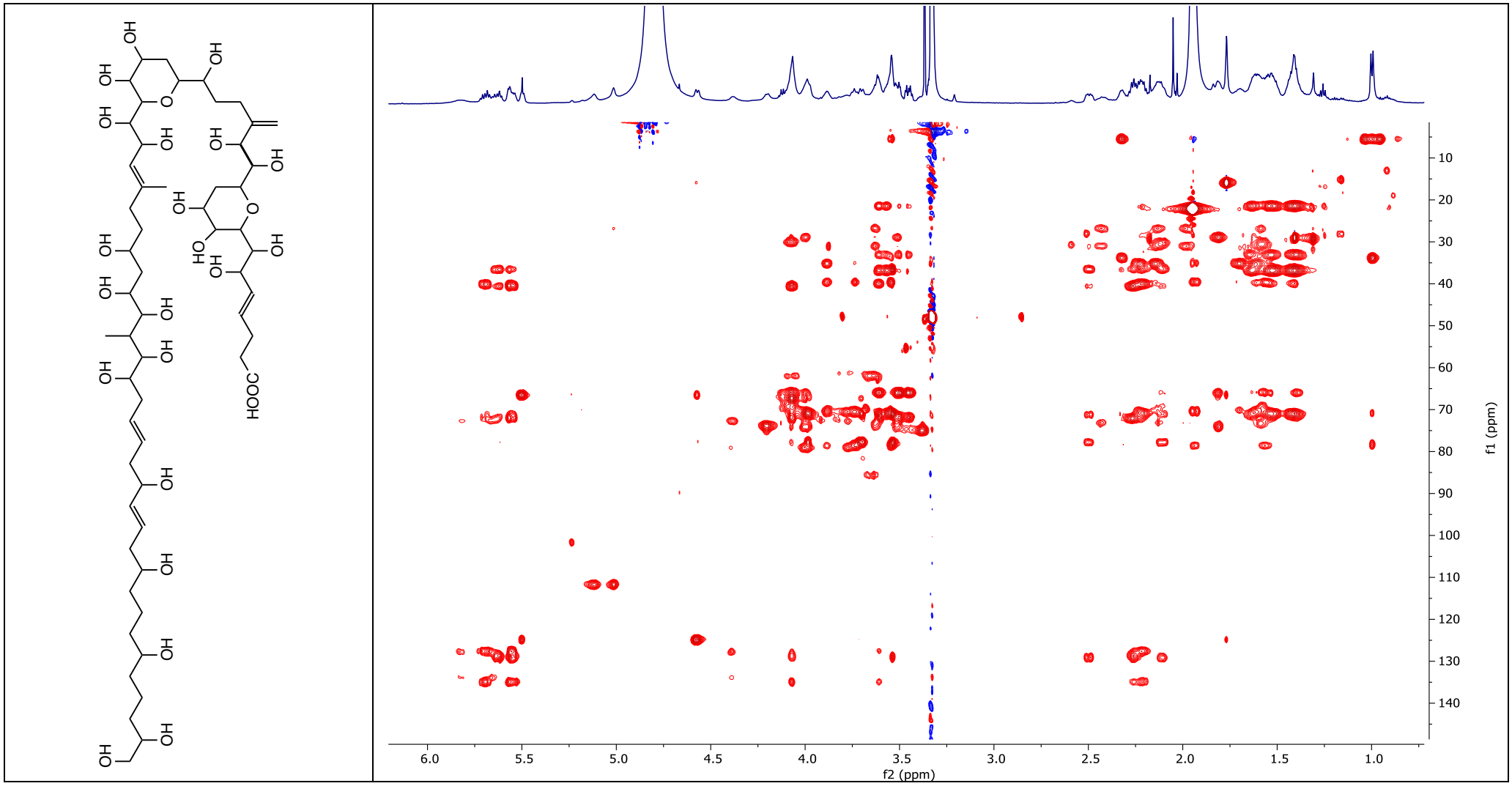


Figure S29. HMBC spectrum (600 MHz, CD_3OD) for amphidinol 26.

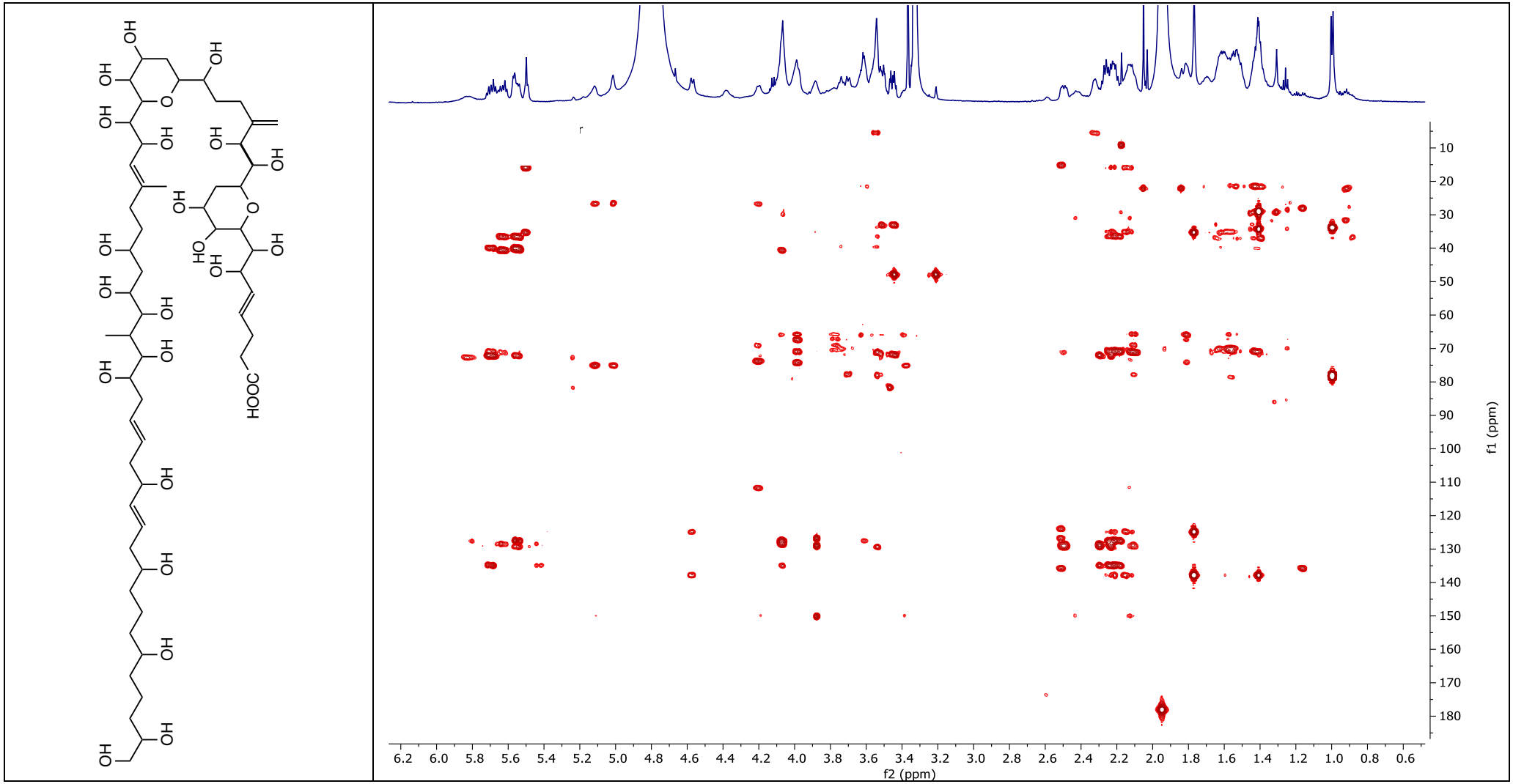


Figure S30. H2BC spectrum (600 MHz, CD_3OD) for amphidinol 26.

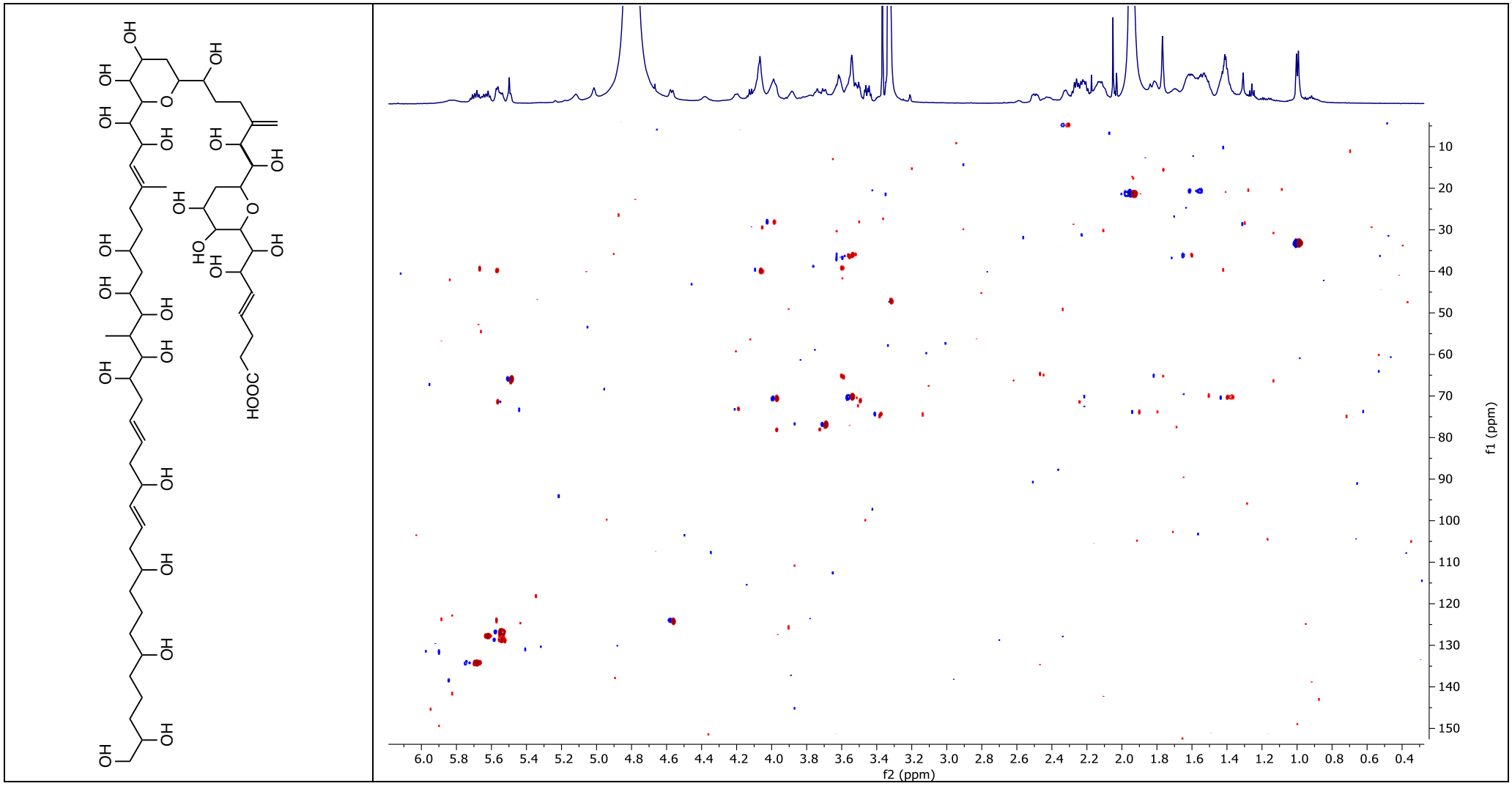


Figure S31. T-ROESY spectrum (600 MHz, CD_3OD) for amphidinol 26.

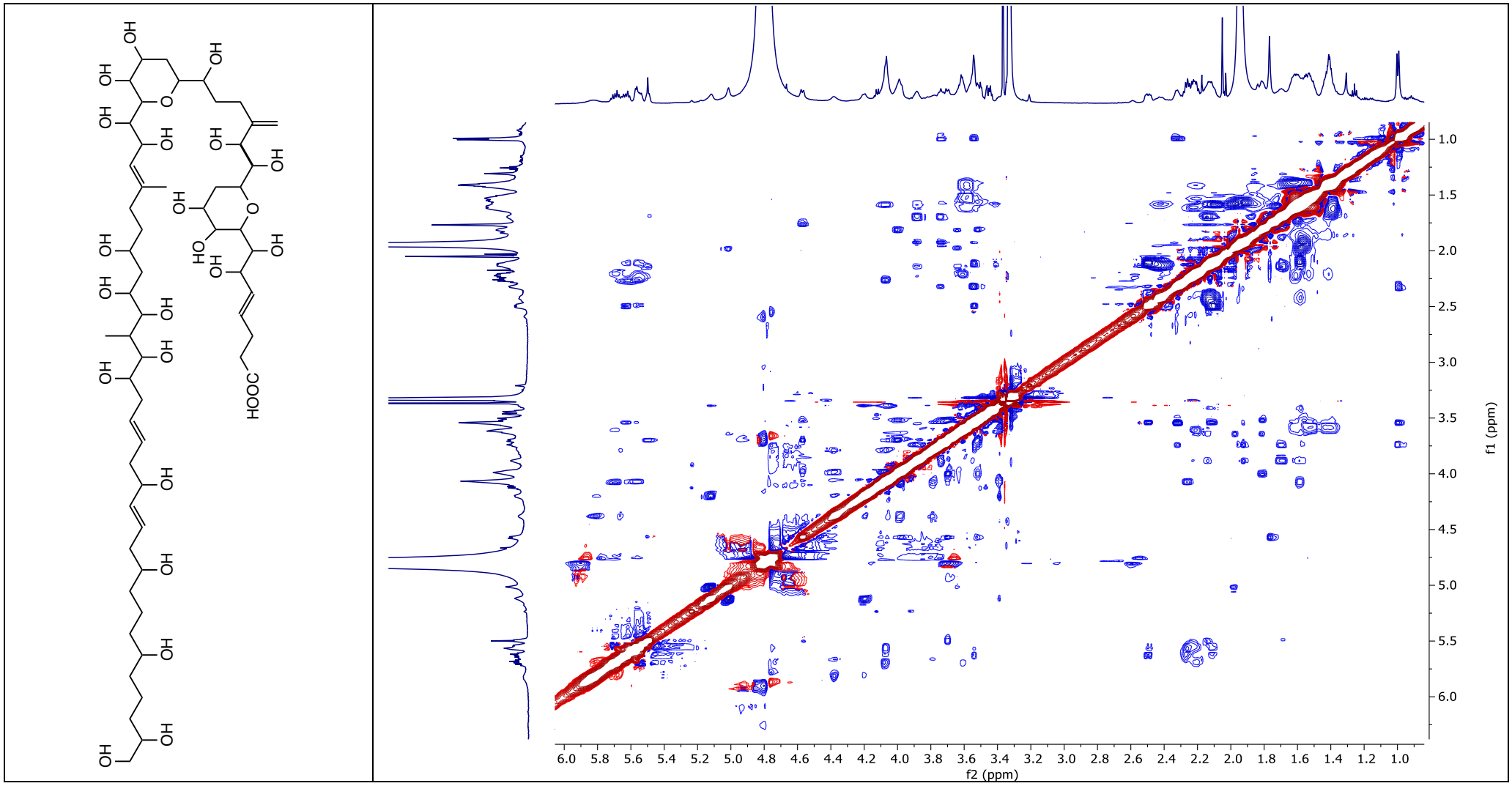


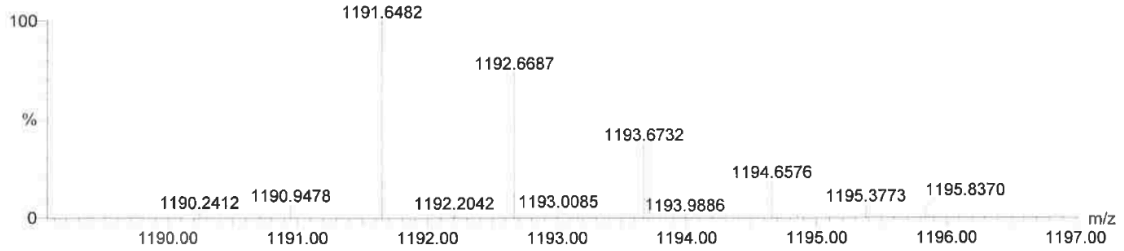
Figure S32. HRESIMS spectrum for amphidinol 26.

Elemental Composition Report **Page 1**

Multiple Mass Analysis: 3 mass(es) processed
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 120.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
325 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-60 H: 0-110 O: 0-25 Na: 0-2
David
ESI (17-159) Adrian (ACO35CI8MAC) 51 (1.778)

2: TOF MS ES+
1.68e+002



Minimum:	20.00				-1.5			
Maximum:	100.00		5.0	5.0	120.0			
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1191.6482	100.00	1191.6526	-4.4	-3.7	10.5	26.5	0.5	C59 H99 O24
		1191.6502	-2.0	-1.7	7.5	27.2	1.3	C57 H100 O24 Na
		1191.6478	0.4	0.3	4.5	28.1	2.2	C55 H101 O24 Na2
1192.6687	73.82	---						
1193.6732	37.73	1193.6683	4.9	4.1	9.5	33.5	0.4	C59 H101 O24
		1193.6787	-5.5	-4.6	7.5	34.4	1.2	C59 H103 O21 Na2

Figure S33. Amphidinol 26 conversion from aldehyde to carboxylic acid at C-54 observed by ESI-HRMS.

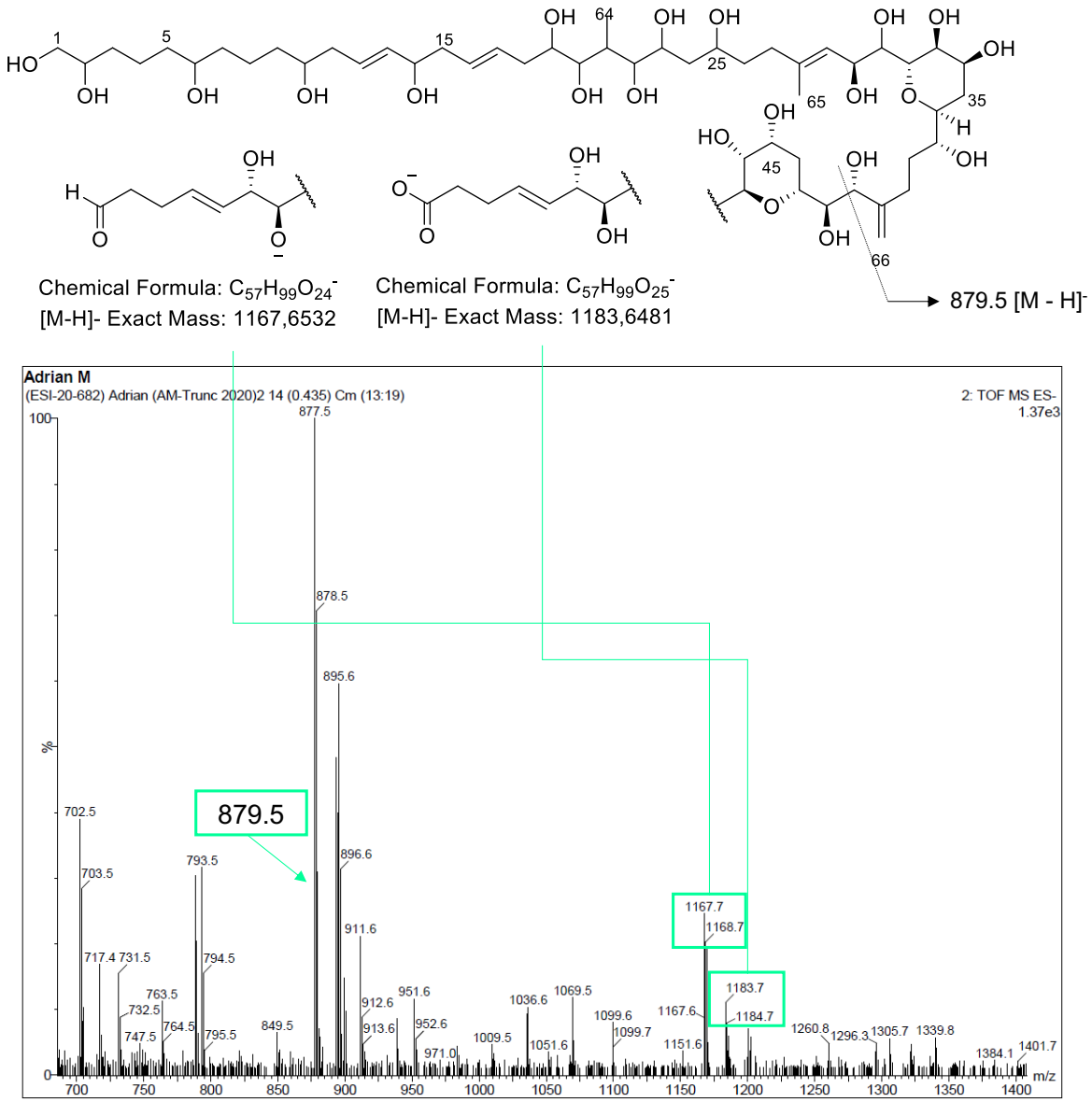


Figure S34. Amphidinol 26 single mass composition analysis for aldehyde and carboxylic states.

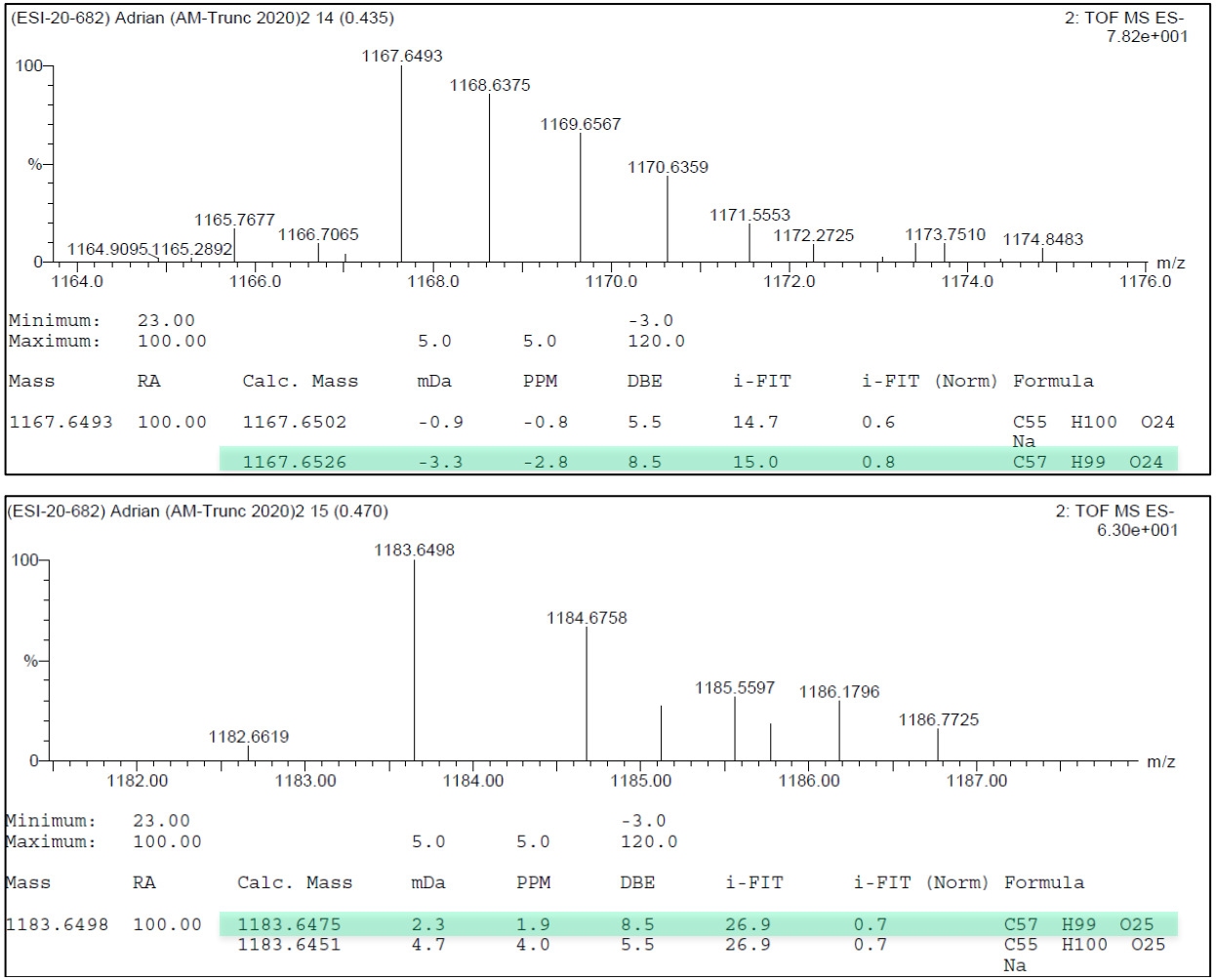
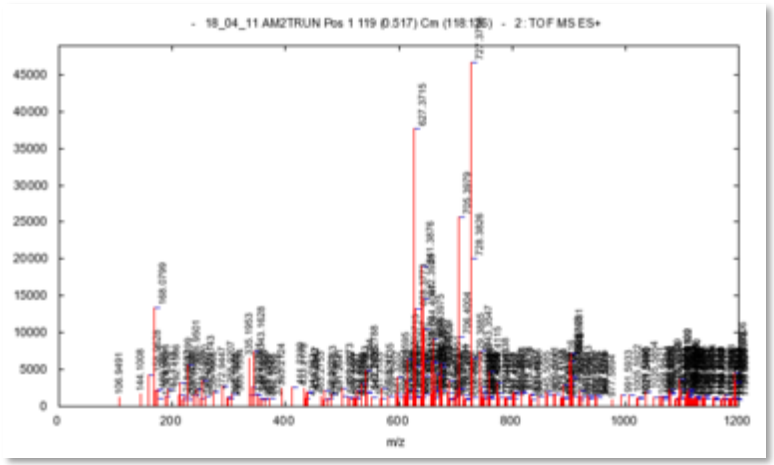


Figure S35. Main MS/MS fragments observed for amphidinol 26 as aldehyde.



ID	*m/z*	Formula	Calc.	Deviation	Losses	Add.	Score	Bonds
1	1153.6769	$C_{57}H_{101}O_{23}$	1153.6743	+ 3.4 mDa	- O	+ 2H	0.5	1
2	1140.6281	$C_{55}H_{96}O_{24}$	1140.6292	- 1.1 mDa	- C_2H_5	+ 0H	2.0	2
3	1111.6271	$C_{54}H_{95}O_{23}$	1111.6264	+ 0.7 mDa	- C_3H_6O	+ 0H	1.0	1
4	1109.6536	$C_{55}H_{97}O_{22}$	1109.6471	+ 6.5 mDa	- $C_2H_4O_2$	+ 2H	1.0	1
5	1077.5829	$C_{53}H_{89}O_{22}$	1077.5845	- 1.6 mDa	- $C_4H_{12}O_2$	- 1H	2.0	0
6	1065.5861	$C_{52}H_{89}O_{22}$	1065.5845	+ 1.6 mDa	- $C_5H_{12}O_2$	+ 0H	1.0	1
7	949.5388	$C_{47}H_{81}O_{19}$	949.5372	+ 1.2 mDa	- $C_{10}H_{20}O_5$	+ 3H	1.5	2
8	923.4917	$C_{44}H_{75}O_{20}$	923.4852	+ 8.3 mDa	- $C_{13}H_{26}O_4$	+ 0H	1.0	1
9	891.4882	$C_{44}H_{75}O_{18}$	891.4953	- 7.1mDa	- $C_{13}H_{26}O_6$	- 1H	2.0	2
10	805.4586	$C_{40}H_{69}O_{16}$	805.4586	- 6.9 mDa	- $C_{17}H_{32}O_8$	- 1H	2.0	2
11	729.3885	$C_{35}H_{58}O_{15}$	729.3909	- 2.4 mDa	- $C_{24}H_{40}O_7$	+ 3H	2.0	2

ID	*m/z*	Formula	Calc.	Deviation	Losses	Add.	Score	3onds
12	728.3831	$C_{33}H_{60}O_{17}$	728.3831	- 0.5 mDa	- $C_{24}H_{41}O_7$	+ 2H	2.0	2
13	688.3976	$C_{35}H_{59}O_{13}$	687.3956	- 0.5 mDa	- $C_{22}H_{42}O_{11}$	- 1H	2.0	2
14	629.3107	$C_{31}H_{49}O_{13}$	629.3173	- 6.6 mDa	- $C_{26}H_{52}O11$	- 1H	1.5	2
15	581.3202	$C_{27}H_{49}O_{13}$	581.3173	+ 2.9 mDa	- $C_{30}H_{52}O_{11}$	+ 3H	2.0	2
16	581.3202	$C_{27}H_{49}O_{13}$	581.3173	+ 2.9 mDa	- $C_{30}H_{52}O_{11}$	+ 1H	2.0	2
17	481.2649	$C_{22}H_{41}O_{11}$	481.2649	- 0.8 mDa	- $C_{35}H_{60}O_{13}$	+ 1H	2.0	2
18	372.1876	$C_{18}H_{28}O_8$	372.1784	+ 9.2 mDa	- $C_{39}H_{73}O_{16}$	- 2H	2.0	2
19	357.1827	$C_{18}H_{29}O_7$	357.1913	- 8.6 mDa	- $C_{39}H_{72}O_{17}$	+ 1H	1.5	2
20	305.1554	$C_{14}H_{25}O_7$	305.1554	- 4.6 mDa	- $C_{43}H_{76}O_{17}$	+ 3H	1.5	2
21	187.1318	$C_{10}H_{19}O_3$	187.1334	- 1.6 mDa	- $C_{47}H_{82}O_{21}$	- 1H	1.5	2
22	169.0852	$C_9H_{13}O_3$	169.0865	- 1.3 mDa	- $C_{48}H_{88}O_{21}$	- 1H	2.0	2

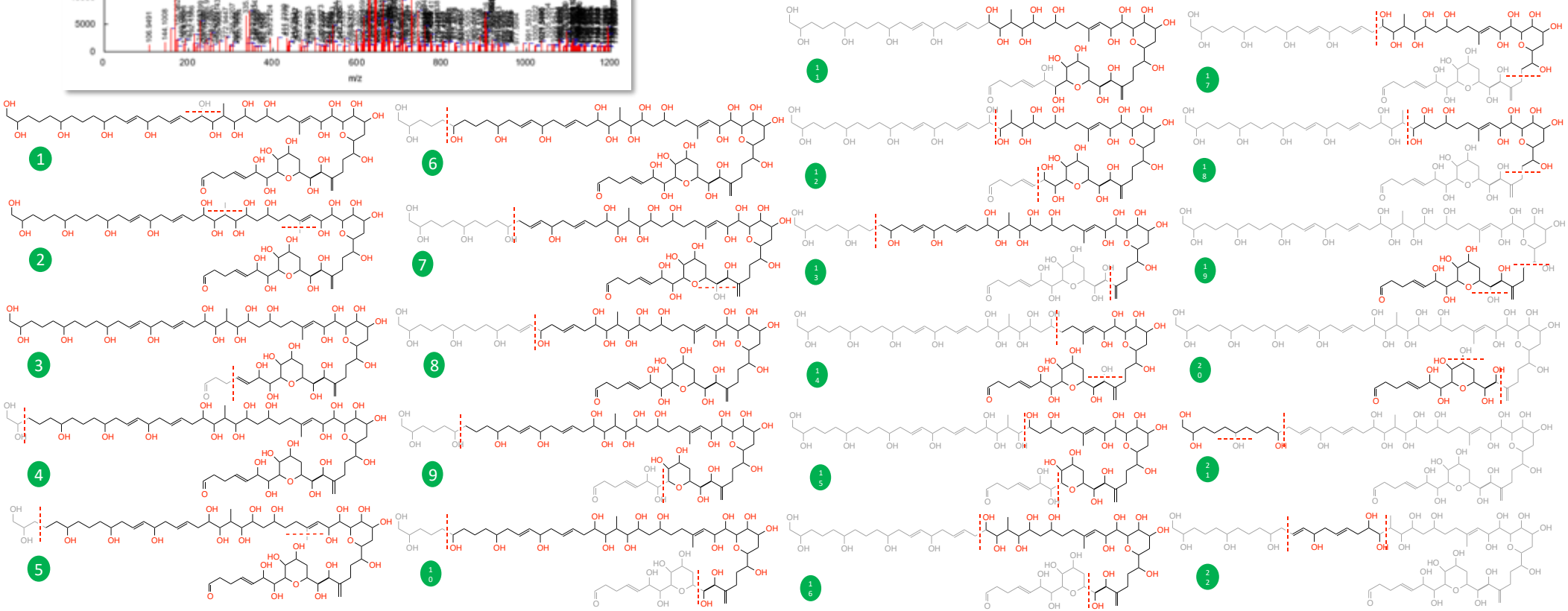


Figure S36. ^{1}H-NMR and HSQC$_{ed}$ spectra (600 MHz, CD_3OD) for luteophanol D.

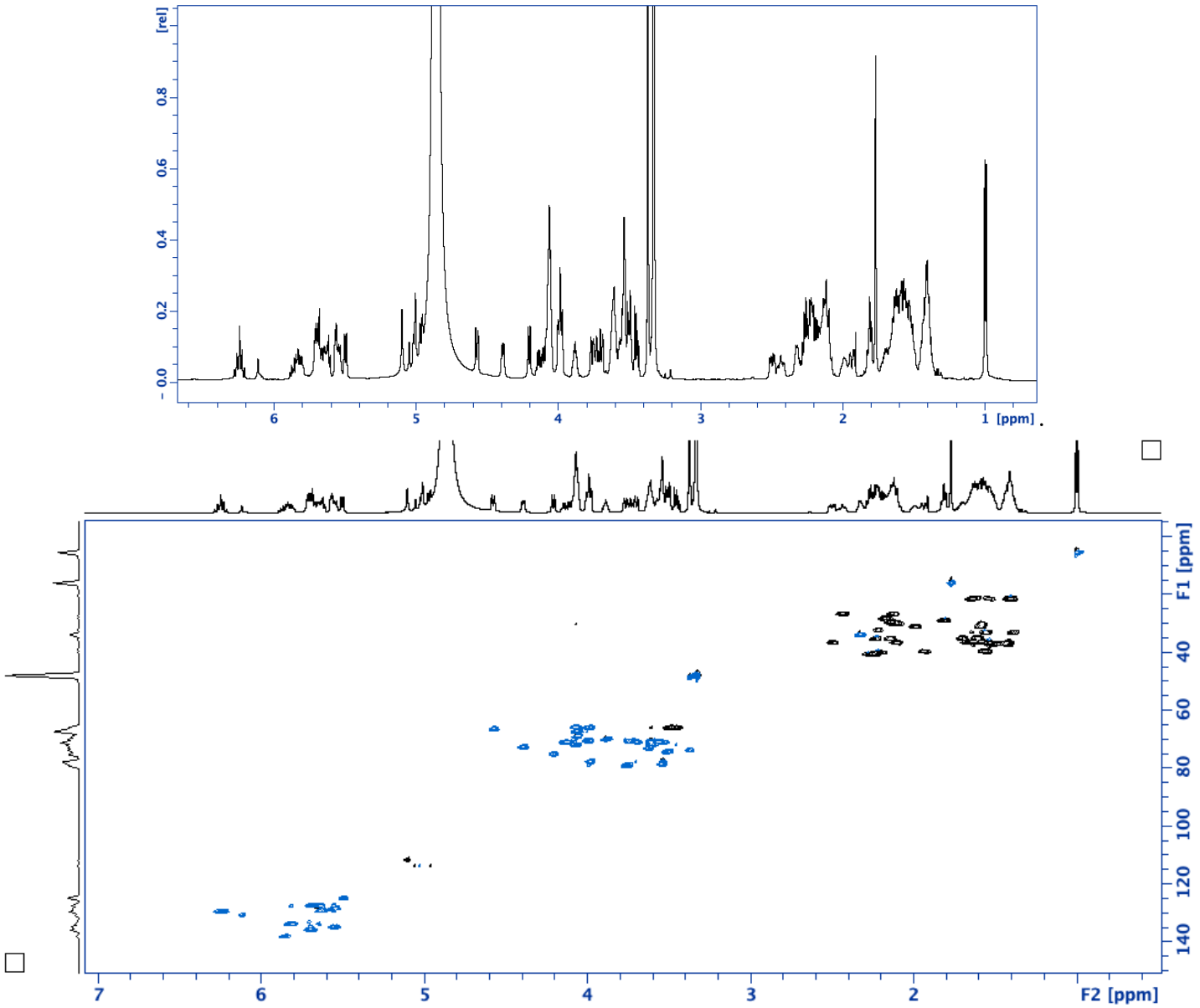
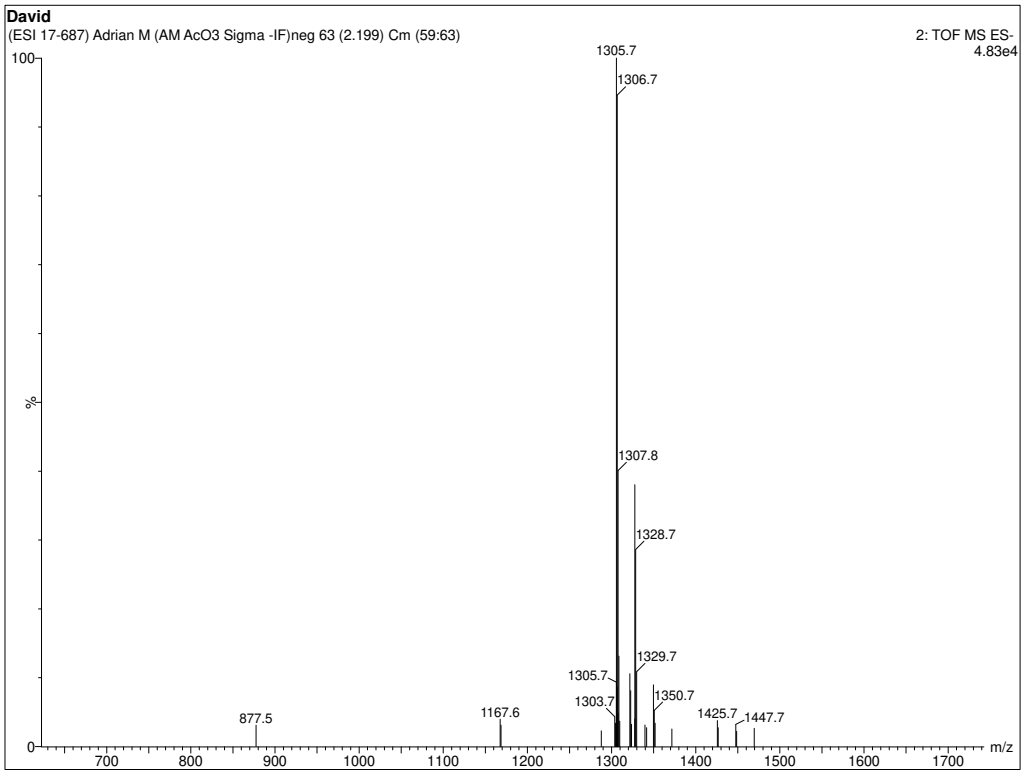


Figure S37. HRESIMS spectrum for luteophanol D.

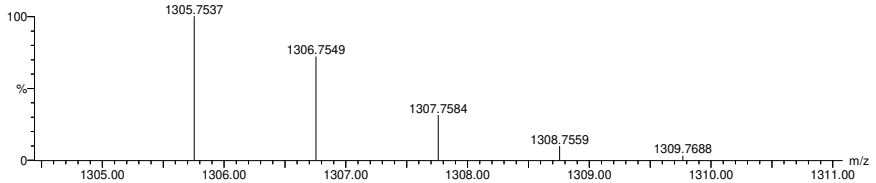


Elemental Composition Report **Page 1**

Multiple Mass Analysis: 3 mass(es) processed
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
906 formula(e) evaluated with 9 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-80 H: 0-120 O: 0-30 Na: 0-1

David
(ESI 17-687) Adrian M (AM AcO3 Sigma -IF)neg 94 (3.279)
2: TOF MS ES-
5.24e+003



Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
Minimum:	20.00				-1.5			
Maximum:	100.00		5.0	5.0	100.0			
1305.7537	100.00	1305.7547	-1.0	-0.8	7.5	10.8	0.0	C64 H114 O25 Na
		1305.7571	-3.4	-2.6	10.5	14.0	3.3	C66 H113 O25
		1305.7512	2.5	1.9	19.5	16.6	5.9	C73 H109 O20
		1305.7488	4.9	3.8	16.5	16.7	5.9	C71 H110 O20 Na
1306.7549	71.82	---						
1307.7584	31.12	1307.7575	0.9	0.7	5.5	20.6	1.0	C62 H115 O28
		1307.7551	3.3	2.5	2.5	20.7	1.0	C60 H116 O28 Na
		1307.7586	-0.2	-0.2	24.5	21.5	1.8	C78 H108 O15 Na
		1307.7610	-2.6	-2.0	27.5	22.2	2.5	C80 H107 O15
		1307.7645	-6.1	-4.7	15.5	23.2	3.5	C71 H112 O20 Na

Figure S38. ^{1}H-NMR and HSQC$_{ed}$ spectra (600 MHz, CD_3OD) for amphidinol 20B.

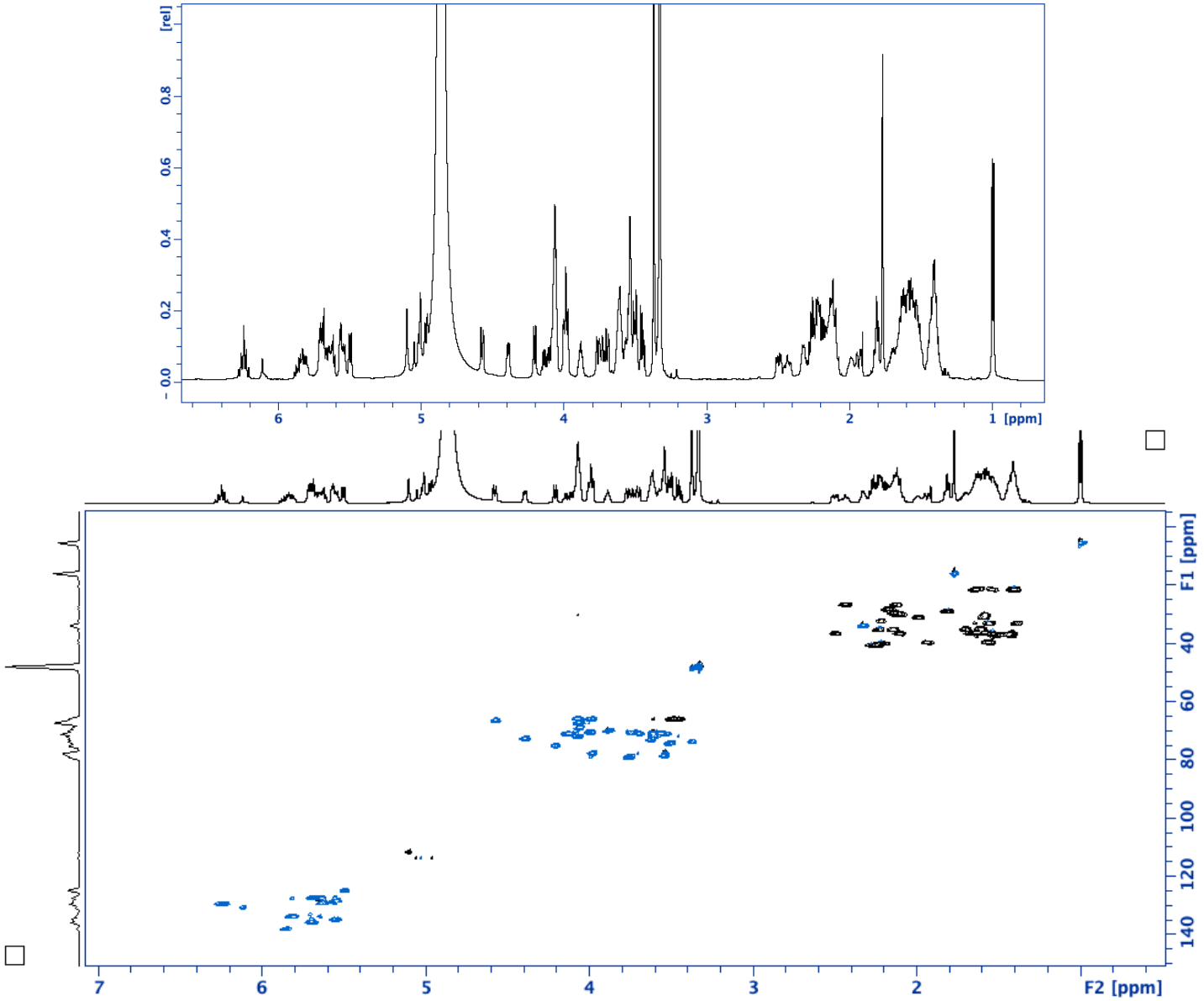
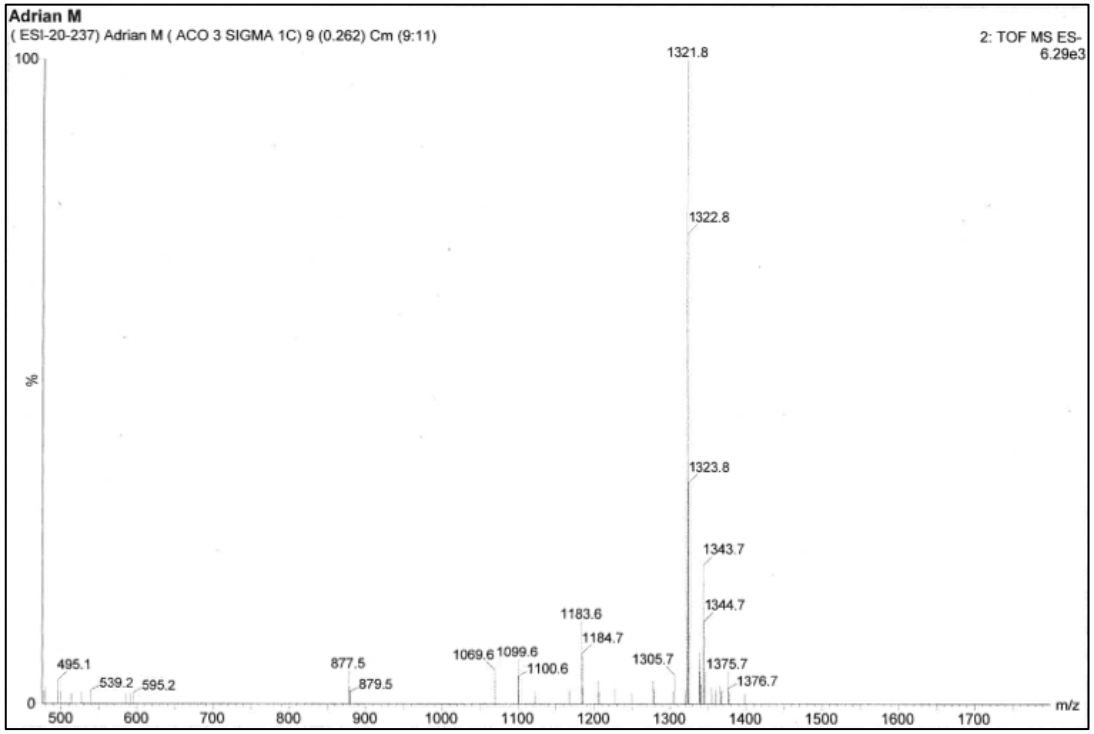


Figure S39. HRESIMS spectrum for amphidinol 20B.

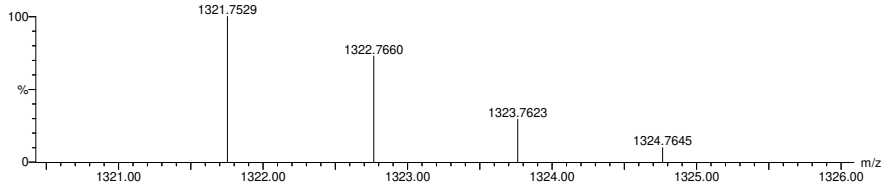


Elemental Composition Report **Page 1**

Multiple Mass Analysis: 3 mass(es) processed
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
847 formula(e) evaluated with 8 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-80 H: 0-120 O: 0-30 Na: 0-1

Adrian M
(ESI-20-237) Adrian M (ACO 3 SIGMA 1C) 34 (1.462)
1: TOF MS ES-
9.11e+002



Minimum:	20.00				-1.5				
Maximum:	100.00		5.0	5.0	100.0				
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
1321.7529	100.00	1321.7496	3.3	2.5	7.5	13.1	0.7	C64 H114 O26 Na	
		1321.7520	0.9	0.7	10.5	13.2	0.8	C66 H113 O26	
		1321.7590	-6.1	-4.6	20.5	15.8	3.4	C75 H110 O18 Na	
1322.7660	72.80	---							
1323.7623	29.39	1323.7653	-3.0	-2.3	6.5	22.9	1.5	C64 H116 O26 Na	
		1323.7618	0.5	0.4	18.5	23.0	1.5	C73 H111 O21	
		1323.7594	2.9	2.2	15.5	23.0	1.6	C71 H112 O21 Na	
		1323.7677	-5.4	-4.1	9.5	23.1	1.6	C66 H115 O26	
		1323.7559	6.4	4.8	27.5	23.3	1.9	C80 H107 O16	